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THE INVESTIGATION OF THE DECOMPOSITION OF DIAZONIUM SALTS IN AQUEOUS SOLUTION

A THESIS

Presented to

The Faculty of the Graduate Division

by

Benjamin Dennis Smith

In Partial Fulfillment

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Doctor of Philosophy

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June, 1966

THE INVESTIGATION OF THE DECOMPOSITION OF

DIAZONIUM SALTS IN AQUEOUS SOLUTION

Approved:

Chairman

Date Approved by Chairman: 18 May, 1966

To my parents

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GLOSSARY OF ABBREVIATIONS

A	absorption
A_{INF}	infinity absorption
A_{INT}	initial absorption
AL	least squares absorption value
A_T	experimental absorption value
BD	initial concentration of the diazonium salt
BL	least squares constant
c	concentration (moles per liter)
°C	degrees centigrade
cm	centimeter
δ	absorption, parts per million (ppm.)
Diaz.	diazonium salt
DIF	mathematical variable
e	extinction coefficient
e_{BA}	extinction coefficient of molecular complex
gr.	grams
HOAc	acetic acid
H_3PO_4	phosphoric acid
k	rate constant
K_{BA}	equilibrium constant for molecular complex
KH_2PO_4	monobasic potassium phosphate
J	coupling constant, cycles per second
KHP	potassium acid phthalate

KI	potassium iodide
KL	least squares rate constant
l	light path through the solution
LT	mathematical variable
M	molarity, moles of solute per liter of solvent
m-	meta
mm. of Hg	millimeters of mercury
ml.	milliliters
mμ	millimicrons
n-	normal
N	number of data points
NaOAc	sodium acetate
p-	para
pH	$= -\log_{10} a_{H(+)}$ (puissance d'hydrogen)
Rad.	Radical
σ	sigma
t	time
TA	initial concentration of tertiary amine
TMPD	N,N,N'N' - tetramethyl-p-phenylenediamine
$TMPD^{(+)}$	Wurter's Blue Cation, radical cation
μ	micron
UV	ultraviolet

CHAPTER I

INTRODUCTION

Since the discovery of aromatic diazo compounds in 1858 by Peter Griess, a large variety of reactions employing the aromatic diazo compounds as the starting material has occupied the research efforts of a small army of chemists. Some such reactions occur without loss of nitrogen, for example the reduction of diazonium salts to hydrazines, and diazo coupling. Coupling reactions occur with activated aromatic compounds, phenols and aromatic amines, as well as with activated methylene groups. Others result in the replacement of the diazonium group by another functional group. Examples of these reactions, yielding a variety of products, include numerous "name reactions" such as the Sandmeyer, Schiemann and Meerwein reactions. Benzyne intermediates may be formed if an easily lost group occupies the ortho position. Nucleophilic displacement of groups such as the nitro group and halide ions which have been activated by a diazonium group in the ortho or para positions may occur.

The utility of these reactions lies in the fact that the diazonium salts are easily accessible substances and undergo the above-named reactions under relatively mild, although diverse, conditions without the necessity of other activating groups.

These reactions have been the subject of several excellent discussions. In his classical work, K. H. Saunders discusses the reactions from a preparative point of view.[1] W. A. Waters[2] and H. Zollinger[3] have

treated the reactions according to reaction mechanisms. The possible free radical nature of some of these reactions has been reviewed by W. A. Waters,[4] C. Walling[5] and G. Sosnovsky.[6]

The work with which this thesis is concerned had its beginning in the attempt to study the details of a reaction which was thought to be of the type in which the carbon-nitrogen bond is cleaved. A priori, both homolytic and heterolytic pathways must be considered as possible courses for such a reaction. Each major type may be subdivided according to whether the diazonium salt reacts singularly or first reacts with a second species. Some possibilities are given by the general equations 1 through 7. One through 3 represent homolytic processes, and 4 through 7 represent heterolytic processes.

$$Ar\text{-}N_2^{(+)} \longrightarrow Ar^{\cdot} + {}^{\cdot}N_2^{(+)} \qquad \text{(Eq. 1)}$$

$$Ar\text{-}N_2^{(+)} + :B \rightleftharpoons ArN_2B^{(+)} \qquad \text{(Eq. 2)}$$

$$ArN_2B^{(+)} \longrightarrow Ar^{\cdot} + N_2 + {}^{\cdot}B^{(+)} \qquad \text{(Eq. 3)}$$

---

[1]K. H. Saunders, "The Aromatic Diazo-Compounds and Their Technical Applications," 2nd ed., E. Arnold and Co., London, 1949.

[2]W. A. Waters, J. Chem. Soc., 1942, 266.

[3]H. Z. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," Interscience Publishers, Inc., New York, 1961.

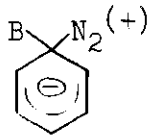
[4]W. A. Waters, "Chemistry of Free Radicals," 2nd ed., Oxford University Press, Amen House, London, 1946, p. 146.

[5]C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, 1957, pp. 518-522.

[6]G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," The MacMillan Company, New York, 1964, p. 181.

$$ArN_2^{(+)} \longrightarrow Ar\cdot^{(-)} + N_2^{(+2)} \qquad \text{(Eq. 4)}$$

$$ArN_2^{(+)} \longrightarrow Ar^{(+)} + N_2 \qquad \text{(Eq. 5)}$$

$$ArN_2^{(+)} + :B^{(-)} \longrightarrow \text{  } \qquad \text{(Eq. 6)}$$

$$\text{  } \longrightarrow ArB + N_2 \qquad \text{(Eq. 7)}$$

The product given by Eq. 2, $ArN_2B^{(+)}$, may represent either a sigma- or a pi-complex. In a sigma-complex the terminal nitrogen atom of the diazonium group would be bonded to a single atom of the electron donor species, :B. For instance, if the electron donor species is a primary or secondary amine, a single bond is established between the amine nitrogen and the terminal diazo nitrogen; from this complex a stable diazoamino compound can be formed with the loss of a proton. In reactions catalyzed by copper salts an association between the terminal nitrogen and the metal cation may occur to give an intermediate which may decompose to radical species or by a cyclic process to give the product directly.[3] If the electron donor, :B, is an aromatic compound, then the pi-electron clouds of the diazonium salt and the electron donor may interact to form a molecular complex with the two aromatic nuclei in parallel planes. Experimental evidence for these possibilities will be reviewed later.

The homolytic pathway according to Eq. 2 and Eq. 3 is generally accepted for reactions occurring under basic and nonpolar conditions. The two heterolytic pathways according to Eq. 5 and to Eqs. 6 and 7 are

generally cited for reactions occurring under acidic and polar solvent conditions. The possibilities given by Eq. 1 and Eq. 4 may be discarded due to the high energy requirements of forming nitrogen with one and two formal positive charges.

The possibility that homolytic cleavage can occur under certain conditions in acidic polar medium has not been extensively considered by previous research workers. Cox, Gladys, Field and Pearson[7] suggested that both a heterolytic and homolytic process occurred when they reacted a variety of diazonium salts with potassium ethylxanthate. The homolytic cleavage of an intermediate diazo thioether has been suggested to be responsible for the large rate enhancement which is observed with the decomposition of N,N-dicyclohexylbenzamide-o-diazonium tetrafluoroborate.[8] The possibility that an aryl radical is produced from an initial reduction by iodide has been suggested by several workers.[4,8,9]

Our experiments were designed, therefore, to attempt to define the scope and importance of such reaction pathways in diazonium replacements in acidic solution. In the hope of trapping free radical intermediates produced by homolytic cleavage, the diazonium salts were decomposed in the presence of easily oxidized free radical precursors such as N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD). Preliminary studies of the reaction given by Eq. 8 showed the rate of production of the colored radical-ion formed from the diamine to be much larger than the rate of evolution of

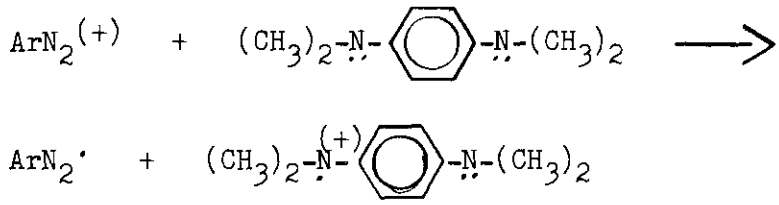
---

[7]J. R. Cox, Jr., C. L. Gladys, L. Field and D. E. Pearson, J. Org. Chem., 25, 1083 (1960).

[8]J. Lipowitz and T. Cohen, J. Org., Chem., 30, 3891 (1965).

[9]E. S. Lewis and M. D. Johnson, J. Am. Chem. Soc., 82, 5408 (1960).

nitrogen from the diazonium salt in the absence of the diamine.



(Eq. 8)

These preliminary results suggested a one-electron transfer reaction to be taking place. An investigation of this reaction was deemed to be important for two primary reasons. First, the investigation would hopefully help to clarify the nature of the homolytic cleavage of the carbon-nitrogen bond. Secondly, electron transfer reactions in organic chemistry are rare and a study of a clear example may be expected to be rewarding.

At this point, a review of the literature covering various aspects of this reaction would be helpful.

CHAPTER II

LITERATURE EVIDENCE FOR ONE-ELECTRON TRANSFER AND FREE RADICAL REACTIONS OF DIAZONIUM SALTS

Reactions with Amines

The reaction between TMPD and the 4-dimethylaminobenzenediazonium cation has been recently reported to give the Wurster's Blue Cation, the oxidized cation of TMPD, in oxygen-free basic solution.[10,11] This reaction could proceed by pathways described by Eq. 2 and Eq. 3. Whether in such a reaction $ArN_2B^{(+)}$ exists as a distinct species with a nitrogen-nitrogen sigma bond, as an intermediate charge transfer complex, or merely as a transition state, yielding the free radicals of the diazonium salt and $TMPD^{(+)}$ (Wurster's Blue Cation), would depend on the substituent groups of the diazonium salt and the reaction conditions.

The reaction between diazonium salts and primary or secondary amines giving the diazoamino compounds is well documented.[3] The stable products are formed with loss of a proton or of sulfur trioxide if a sulfamic acid is used.[12] The tautomerism of diazoamino compounds prepared from various aryl primary amines has been investigated.[13] In acidic

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[10]P. J. Zandstra and E. M. Evleth, J. Am. Chem. Soc., 86, 2664 (1964).

[11]However, we have found TMPD to be unstable in basic solutions; and, therefore, the accuracy of these results is questionable.

[12]D. Z. Zavel'ski and L. A. Lishnevskaya, J. of Gen. Chem., U.S.S.R., 28, 2602 (1958).

[13]T. Mitsuhashi and O. Simdura, Chemistry and Industry (London), 1964, 578.

solutions, these diazoamino compounds rearrange by an intermolecular process to the thermodynamically more stable aminoazo isomers.

The reaction between diazonium salts and tertiary amines other than TMPD has not been extensively investigated except for coupling reactions to give the aminoazo compounds. However, TMPD has been used as an electron donor to form charge transfer complexes with other electron acceptors. These complexes can decompose to give radical species, depending on the reaction conditions and the electron acceptor.[14] The electron spin resonance spectra[15] and the optical absorption spectra[16] of the complexes with TMPD as the donor and chloranil as the acceptor indicate that free radical ions are produced in the polar solvent, acetonitrile, but not in the non-polar solvents, dioxane and benzene. Experimental evidence for the formation of the charge transfer complex as combining TMPD as electron donor with ten different dinitronaphthalenes[17] and numerous other compounds as electron acceptors[18] has recently been presented.

For the purpose of discussion of the results obtained with the reaction between the various diazonium salts and TMPD, studies of complex formation with electron acceptors having a nitro group in place of the

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[14]L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, 1964, pp. 15-31, 44-77.

[15]I. Isenberg and S. L. Baird, Jr., J. Am. Chem. Soc., 84, 3803 (1962).

[16]J. W. Eastman, G. Engolsma and M. Calvin, J. Am. Chem. Soc., 84, 84, 1339 (1962).

[17]P. H. Emslie and R. Foster, Tetrahedron, 1964, 1489.

[18]R. Foster and T. J. Thomson, Faraday Society Transactions (London), 59, 2287 (1963).

diazonium group would be the most relevant. The acceptor 1,4-dinitrobenzene, to be compared with p-nitrobenzenediazonium tetrafluoroborate, shows free radical formation in methanol but charge-transfer complexes in acetonitrile.[19] Unfortunately, data do not exist to allow comparisons to be made for the other diazonium salts used in the kinetic study.

Reactions with Reducing Reagents

The reduction of diazonium salts can occur by a number of reaction pathways. These pathways cannot be clearly defined at this time because the experimental evidence is very confusing, but both radical and ionic pathways are believed to be important. The radical pathways are usually said to be initiated by a one-electron reduction to give the phenyl radical, although the pathways may be complicated by a caged, radical pair or a cyclic mechanism. There are several reaction pathways which could best explain the ionic reactions. These possibilities include a cyclic mechanism, a caged ion pair mechanism and a hydride shift mechanism. Several examples of each type have been chosen for a detailed discussion to illustrate the possible reaction pathways.

Examples of radical reactions which are believed to be initiated by an electron transfer reaction include the reductions by hypophosphorous acid,[20,21] by ethanol in the presence of zinc,[22,23] and by

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[19]R. Foster and T. J. Thomson, Faraday Society Transactions (London), 59, 1059 (1963).

[20]N. Kornblum, "Organic Reactions," vol. II, John Wiley and Sons, New York, 1944, p. 262.

[21]N. Kornblum, G. D. Cooper and J. E. Taylor, J. Am. Chem. Soc., 72, 3013 (1950).

methanol in the presence of acetate buffer but in the absence of oxygen,[24,25] and by the iodide anion,[9] although these reactions could involve the formation of benzenediazonium tri-iodides.[26,27]

The characteristics of the reaction between hypophosphorous acid and the diazonium salts are illustrated by Kornblum's experimental results.[21] Although an effort was made to exclude oxygen and to insure identity of the reaction conditions, in no instance could reproducible results be obtained. He found that trace amounts of certain oxidizing agents, such as copper sulfate, potassium dichromate and permanganate, showed a very different behavior with this diazonium salt. The reaction was strongly catalyzed for a few minutes and then completely inhibited for a considerable time. The inhibition of the reaction was explained by the formation of a quinone or a semiquinone from the diazonium salt or its reaction product by the oxidizing agent. The addition of these compounds to the reaction mixture was found to inhibit the reduction reaction.

While the experimental results did not permit a clear definition for the complex chain of events involved in this reaction, Kornblum did feel that the experimental results were consistent with a free radical

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[22]A. Roe and J. R. Graham, J. Am. Chem. Soc., 74, 6297 (1952).

[23]P. S. Johnson and W. A. Waters, J. Chem. Soc., 1962, 4652.

[24]DeLos F. DeTar and M. N. Turetzky, J. Am. Chem. Soc., 78, 3925 (1955).

[25]DeLos F. DeTar and T. Kosuge, J. Am. Chem. Soc., 80, 6072 (1958).

[26]J. G. Carey and I. T. Millar, Chemistry and Industry (London), 1960, 97.

[27]J. G. Carey, G. Jones and I. T. Millar, Chemistry and Industry (London), 1959, 1018.

pathway. The radical-chain initiation step was said to be an electron transfer reaction followed by formation of the radical species according to Eqs. 2 and 3. This was said to be followed by a chain propagation step where the aromatic radical reacts with a second mole of the hypophorous acid to give the observed reduction product of the diazonium salt and a stable radical from the hypophosphorous acid. The proposed reaction pathway is illustrated by Eqs. 9-12.

$$Ar\text{-}N_2^{(+)} + H_3PO_2 \rightleftharpoons ArN_2PO_2H_2 + H^{(+)} \qquad \text{(Eq. 9)}$$

$$ArN_2PO_2H_2 \rightleftharpoons Ar\cdot + N_2 + (H_2PO_2)\cdot \qquad \text{(Eq. 10)}$$

$$Ar\cdot + H_3PO_2 \longrightarrow ArH + (H_2PO_2)\cdot \qquad \text{(Eq. 11)}$$

$$ArN_2 + (H_2PO_2)\cdot \longrightarrow Ar\cdot + N_2 + (H_2PO_2)^{(+)} \qquad \text{(Eq. 12)}$$

The experimental evidence that supports this reaction pathway includes the order of reactivity for the uncatalyzed reduction of the diazonium salts ($4\text{-}O_2N\text{-} > 4\text{-}CH_3\text{-} > 4\text{-}CH_3O\text{-}$), the effect of the oxidizing reagents, and the fact that trace amounts of the more reactive diazonium salts catalytically speed reaction of less reactive salts. The order of reactivity of the diazonium salts is the same order for the ease of formation of the covalent structure according to Eq. 9. Trace amounts of the more reactive diazonium salts could serve to initiate the chain process for the less reactive diazonium salts. The oxidizing reagent could bring about an initial one-electron oxidation of the hypophosphorous acid to yield a more reactive free radical species. The fact that the reaction proceeds at the usual rate in darkness discredits a photo-induced process.

Because of the strong electron withdrawing ability of the diazonium

group, the 4-phenylenetetrazonium ion would be expected to be an excellent electron acceptor. At high iodide concentrations, 4-diiodobenzene is produced; at intermediate iodide concentrations, p-iodobenzenediazonium ion is the chief product, and at still lower concentrations, 4-hydroxybenzenediazonium ion predominates. The oxygen of the p-hydroxybenzenediazonium ion is believed to have been derived from molecular oxygen which was dissolved in the solution. The initiation step which was proposed by Lewis[9] involves the formation of a benzenediazoiodide intermediate which decomposes into a phenyl radical, nitrogen, and the iodide radical. This same one-electron transfer reaction has been proposed by us as the first step in our reactions between TMPD and the diazonium salts, Eq. 8, Eq. 23 and Eq. 24, as well as by Kornblum,[21] as the first step in the reactions between hypophosphorous acid and the diazonium salts, Eq. 9 and Eq. 10. The fate of the phenyl radical depends on the relative concentration of the oxygen which is dissolved in the solution and upon the original concentration of the iodide ion. At high iodide concentrations the phenyl radical is said to react with an iodine radical or with iodine which is formed in solution from two iodine radicals. At lower iodide concentrations the phenyl radical is formed but is not captured in the above manner. Instead, it is said to react with molecular oxygen to form an aromatic peroxide radical which we have also postulated for our TMPD studies, Eq. 31. This intermediate is said to dimerize to give a dimer which can disproportionate into the phenoxy radical and oxygen. The phenoxy radical can react with a proton and an iodide ion to give the observed phenol and an iodine radical. At intermediate iodide concentration the reaction sequence is further com-

plicated by a bimolecular, nucleophilic attack by the iodide ion on the 4-phenylenetetrazonium ion to give the observed 4-iodobenzenediazonium ion.

Reduction reactions under other experimental conditions do not always lead to the formation of free radicals in solution. For example, a number of complexes have been proposed for the reaction between diazonium salts and the ions of the transition elements. A number of such complexes derived from the diazonium chloride of p-aminodimethylaniline show charge transfer interaction properties in the solid state,[28] but not in solution.[29] However, reduction of diazonium salts with other transition elements clearly indicates that an electron transfer has taken place in solution. For example, the stannous cation[20] and the chromous cation[30] will reduce the diazonium salts to the corresponding hydrazines.

Less powerful reagents, such as the cuprous salt and the iodide ion, possess favorable oxidation potentials. These reagents can act to form a radical species by a one-electron transfer reaction. The reactions in which the diazonium group is replaced by a halide or other anion in acidic solution usually require a specific copper catalysis. The Sandmeyer reaction[31,32] requires a cuprous salt, while the Gattermann reaction requires metallic copper. The Meerwein arylation of activated

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[28]E. A. Boudreaux, H. B. Jonassen and L. J. Theriot, J. Am. Chem. Soc., 85, 2039 (1963).

[29]E. A. Boudreaux, H. B. Jonassen and L. J. Theriot, J. Am. Chem. Soc., 85, 2896 (1963).

[30]R. S. Bottel and N. H. Furman, Analytical Chemistry, 29, 119 (1957).

[31]D. C. Nonhebel and W. A. Waters, "Advances in Catalysis," vol. IX, p. 351 (1957)

olefinic compounds is catalyzed by the cupric ion. However, the catalyzing effect of the cupric cation probably arises from its reacting first with the acetone solvent to yield the cuprous cation which then catalyzes the reaction.[33] Reactions carried out under Meerwein reaction conditions include the decomposition of various diazonium salts in the presence of chlorobenzene or nitrobenzene,[34] anthracene,[35] derivatives of maleic and fumaric acids[36] and biphenylene.[37] The products obtained from these reactions all show the characteristic properties of homolytic substitution and thus suggest a free radical pathway. The closely related Pshorr ring closure reaction also proceeds by a radical pathway when a copper catalyst is used.[38,39]

The closely related reactions which give biaryls by the decomposition of N-nitrosoacetanilide, or of diazonium salts in the presence of sodium acetate and acetic anhydride or sodium hydroxide, the Gomberg-Bachmann reaction, all proceed chiefly by a free radical pathway.[37,40-43]

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[32]W. A. Cowdrey and D. S. Davies, J. Chem. Soc., p. S 48 (1949).

[33]C. S. Rondestvedt, "Organic Reactions," vol. XI, John Wiley and Sons, New York, 1960, p. 189.

[34]S. C. Dickerman and K. Weiss, J. Org. Chem., 22, 1070 (1957).

[35]S. C. Dickerman, A. M. Felix and L. B. Levy, J. Org. Chem., 29, 26 (1964).

[36]O. Vogl and C. S. Rondertredt, Jr., J. Am. Chem. Soc., 78, 3799 (1956).

[37]S. C. Dickerman, N. Milstein and J. F. W. McOmie, J. Am. Chem. Soc., 87, 5521 (1965).

[38]DeLos F. DeTar, "Organic Reactions," vol. IX, John Wiley and Sons, New York, 1958, p. 409.

[39]R. A. Abramovitch and G. Tertzakian, Tetrahedron Letters, 1963, 1511.

There are several additional miscellaneous reactions which possibly proceed by a radical pathway. For example, diazonium salts react with a number of phosphorus compounds,[6] including hypophosphorous acid,[21] ethyldichlorophosphine[44] and phosphorus trichloride.[45] Diazonium salts also react with pyridine,[46] aliphatic hydroxylamines,[47] ethers,[2,48] acetone,[2,49] ethyl acetate,[2,50] nitriles[2,50] and dimethylforamide.[51]

Examples of the ionic reactions include the reduction of the diazonium salts with various alcohols under acidic conditions,[25] the reaction between diazonium salts and salts of $B_{10}H_{10}^{-2}$[52] and the thermally induced decomposition of the diazonium salts which are derived from o-amino-N,N-dialkylbenzamides.[8,53,54] The latter reaction has been extensively investigated and will be discussed in detail.

The experimental evidences include product studies, kinetic studies, studies of the influence of the solvent and the presence of other compounds, and an independent synthesis of the proposed intermediate. When N,N-dibenzylbenzamide-o-diazonium tetrafluoroborate is thermally decomposed in an aqueous solution, then the products are, among

---

[40]W. E. Bachmann and R. A. Hoffman, "Organic Reactions," vol. II, John Wiley and Sons, New York, 1944, 224.

[41]P. Miles and H. Suschitzky, Tetrahedron, 18, 1369 (1962).

[42]C. Rüchardt and Ekkehard Merz, Tetrahedron Letters, 1964, 2431.

[43]C. Rüchardt and B. Freudenberg, Tetrahedron Letters, 1964, 3623.

[44]P. Mastalerz, Roczniki Chemi, 36, 1093 (1962).

[45]L. D. Quin and J. S. Humphrey, Jr., J. Am. Chem. Soc., 83, 4124 (1961).

[46]R. A. Abramovitch and J. G. Saha, J. Chem. Soc., 1964, 2175.

others, benzaldehyde and N-benzylbenzamide. Cohen and Lipowitz have suggested that these products arose from the solvolytic cleavage of a stable, intermediate cation. The postulated pathway to form this intermediate involved the loss of nitrogen to form the phenyl-carbonium ion followed by an intramolecular hydride ion transfer from the benzyl function. This intermediate cation was prepared by an independent pathway by reacting benzylidinebenzylamine with benzoyl chloride followed by the addition of antimony pentachloride. If this preparation and the decomposition of the diazonium salt are performed in dry ethylene chloride, then the infrared and nuclear magnetic resonance spectra of the resulting products agree with each other and with the proposed structure of the intermediate. If water is added to these two ethylene chloride solutions, then the same four hydrolysis products are observed. The kinetic studies performed in acetic acid and methanol solutions, both 1.0M in sulfuric acid, gave first-order kinetics over more than three half-lives, and, except for a moderate solvent effect, the rates were substantially the same. The rates were insensitive to p-benzoquinone, hydroquinone, chloranil, nitric oxide, and oxygen when the methanol solvent

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[47]M. A. T. Rogers, J. Chem. Soc., 1956, 2784.

[48]H. Meerwein, H. Allendorfer, P. Beekmann, F. R. Kunert, H. Morschell, F. Pawellek and K. L. Wunderlich, Angewandte Chemie, 70, 322 (1958).

[49]A. K. Ingberman, Dis. Abs., 20, 80 (1959).

[50]W. E. Hanby and W. A. Waters, J. Chem. Soc., 1939, 1792.

[51]S. S. Yaroslavsky, Tetrahedron Letters, 1965, 1503.

[52]M. F. Hawthorne and F. P. Olsen, J. Am. Chem. Soc., 87, 2366 (1965).

[53]T. Cohen, A. H. Dinwoodie and L. D. McKeever, J. Org. Chem., 27, 3385 (1962).

[54]T. Cohen and J. Lipowitz, J. Am. Chem. Soc., 86, 2514-5 (1964).

was used. However, if thiophenol or iodine are added to the methanol reaction mixture, a profound rate of enhancement is observed, approximately a 20 per cent increase for the thiophenol. These workers suggested that this rate enhancement may be due to radical reactions. These radical reactions were said to be initiated by a homolytic cleavage of an intermediate diazo thioether and a reduction of the diazonium ion by the iodide ion, respectively; and, therefore, these reactions would be expected to proceed according to a pathway similar to the ones which have been suggested for the hypophosphorous acid reaction and the reaction between the iodide ion and the 4-phenylenetetrazonium ion. However, product and kinetic studies were not performed for these reactions, and, therefore, the reaction pathway cannot be defined.

Photodecompositions

The photodecomposition of diazonium salts is apparently complicated by secondary reactions. The photolysis of aqueous solutions at pH greater than five of 4-dimethylaminobenzenediazonium chloride gives an electron spin resonance spectrum which has been identified as the p-dimethylaminophenoxy radical.[10] Evidence suggesting that this radical is a secondary product produced from the reaction of the diazonium salt and the photolysis product and not as a result of the primary photochemistry of the system includes the following experimental facts. Irradiation of p-dimethylaminophenol in oxygen-free, basic solution did not produce a species which gives an electron spin resonance spectrum; however, when the above diazonium salt was added to the solution in the dark, a spectrum was noted and finally the Wurster's Blue Cation from

TMPD as well as the phenoxy radical of 2,6-di-t-butyl-4-methyl phenol could be produced by the dark reaction of the diazonium salt with the appropriate electron donor in oxygen-free, basic solution.

The photodecomposition of p- and m-nitrobenzenediazonium salts in aqueous and alcoholic solutions in the presence of free radical trapping reagents has led to support for the widely held belief that the diazonium salts decompose by a carbonium ion formation in acidic aqueous solutions, but a free radical pathway is the predominate pathway in alcoholic solutions. Experimental evidence which supports these conclusions includes the nearly equal yield of nitrobenzene (76.6 per cent) and acetaldehyde (74.1 per cent) and the high yield of the nitroiodobenzenes when the diazonium salts are decomposed in alcohols and alcoholic solutions containing iodine respectively.[55]

When 3,5-dimethylbenzene-1,4-diazooxide is heated or irradiated with ultraviolet light, an intermediate is formed which gives typical products formed by radical decomposition of diazonium salts.[56] For instance, 3,5-dimethyl-4-hydroxybiphenyl is formed when this diazonium salt is reacted in the presence of benzene.

Physical Measurements and Hammett Correlations

The experimental evidence which has been presented in the first three sections of this chapter has been concerned with the results of chemical reactions. Experimental results which have been obtained from physical measurements and Hammett correlations have also contributed to

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[55]W. E. Lee, J. G. Calvert and E. W. Malmberg, J. Am. Chem. Soc., 83, 1928 (1961).

[56]T. Kunitake and C. C. Price, J. Am. Chem. Soc., 85, 761 (1963).

the knowledge of the manner in which the carbon-nitrogen bond is cleaved. The experimental methods which have been used include polarographic studies, electron spin resonance spectra studies, and Hammett correlations.

Kochi[57] investigated the polarographic reduction of diazonium ions. The reduction potential was found to be independent of pH over a range of low pH values, a result consistent with the diazonium ions' being the species undergoing reduction. The reduction products were nonhomogeneous tars which contained nitrogen and mercury. The order of ease of reduction of 4-substituted diazonium ions was $-OCH_3 > -CH_3 > -Cl > -H > -NO_2$.

Kochi interpreted these results in terms of an initial one-electron transfer, affording a phenylazo intermediate, which he assumed to be stabilized by the substituents in the order given. This order is, however, opposite to that observed in the reduction with hypophosphorous acid, and probably is not the order of stability of the proposed series of azo radicals.[58]

Electron spin resonance spectra have been observed for a number of reactions of diazonium salts and azobenzenes and nitrosobenzenes. The nitrosobenzenes and azobenzenes are isoelectronic with the diazonium salts. The reaction between phenylhydroxylamine and nitrosobenzene in basic, deoxygenated, mixed organic solvents produces essentially a quantitative yield of the nitrosobenzene radical-anion in less than 0.5

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[57]J. K. Kochi, J. Am. Chem. Soc., 77, 3208 (1955).

[58]The order of the stability of tetrazenes is discussed in Chapter VII.

seconds.[59] Similar one-electron reductions have been observed for a number of other substituted nitroso- and azobenzenes.[60] The influence of the reaction medium on the fate of the nitrosobenzene radical-anion has been extensively investigated. In ethanol containing sodium hydroxide this radical-anion is rapidly produced, then dimerizes by second-order kinetics (1.40×10^2 l./mole-sec. at $23 \pm 1^\circ$ C) to yield azoxybenzene in 96 per cent yield after protonation and the irreversible loss of the hydroxide ion from the intermediate dimer. That the reaction to produce the azoxybenzene is reversible has been shown to be true in other solvents. In pure dimethyl sulfoxide which is 50 per cent saturated with potassium hydroxide, the addition of azoxybenzene produces the electron spin resonance spectrum of the radical-anion. If this solution is exposed to oxygen, then the electron spin resonance spectrum of the nitrosobenzene radical-anion is destroyed and is slowly replaced by the electron spin resonance spectrum of the nitrobenzene radical-anion.

Electron spin resonance studies of phenylation reactions by the Gomberg reaction and by the use of N-nitrosoacetanilides have led to the identification of the diazotate radical as the long-lived intermediate radical.[61] The method of identification was the comparison of the observed and the computer-calculated electron spin resonance spectra. Both of these reactions lead to the common intermediate, a diazoanhydride, which decomposes to a phenyl radical, nitrogen and a diazotate radical.

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[59]G. A. Russell and E. J. Geels, J. Am. Chem. Soc., 87, 122 (1965).

[60]E. J. Geels, R. Konaka and G. A. Russell, Chemical Communications, (London) 1, 13 (1965).

[61]G. Binsch and C. Ruchardt, J. Am. Chem. Soc., 88, 173 (1966).

Under other reaction conditions, different experimental results have been observed. The electron spin resonance spectrum of the 4-dimethylaminophenoxy radical has been identified as the photolysis product from the reaction between the corresponding phenol and diazonium salt in an aqueous solution.[10]

When benzenediazonium chloride was mixed with pure nitrobenzene in the absence of a catalyst, no electron spin resonance spectrum was observed at room temperature. However, when the mixture was heated at 42° C for ten minutes, such a spectrum was observed. Product ratio studies of the amounts of biphenyl and nitrobiphenyls formed when benzenediazonium fluoroborate was decomposed in mixtures of benzene and nitrobenzene also suggest a radical intermediate. However, homolytic cleavage according to Eq. 1 can be calculated to be energetically unfavorable. Several workers have, therefore, pointed out the possibility that a ground state triplet cation is formed in the primary process, thereby accounting for the observed electron spin resonance spectra.[62-64]

Taft[64-66] has given a detailed discussion of the experimental evidence which supports the radical cation as an intermediate. The details of his arguments will be given in the following chapter since the

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[62]B. I. Liogonkii, L. S. Lyubchenko, A. A. Berlin, L. A. Blyumenfel'd and V. P. Parini, Vysokomolekulyarnye Soedineniya, 2, 1494 (1960).

[63]R. A. Abramovitch, W. A. Hymers, J. B. Rajan and R. Wilson, Tetrahedron Letters, 1963, 1507.

[64]R. W. Taft, I. R. Fox and I. C. Lewis, J. Am. Chem. Soc., 83, 3349 (1961).

[65]R. W. Taft, J. Am. Chem. Soc., 83, 3350 (1961).

[66]R. W. Taft, S. Ehrenson, I. C. Lewis and R. C. Glick, J. Am. Chem. Soc., 62, 1400 (1940).

radical cations are said to be important in the thermal, aqueous decomposition of substituted benzenediazonium salts.

CHAPTER III

LITERATURE EVIDENCE CONCERNING THE DECOMPOSITION OF DIAZONIUM SALTS IN THE ABSENCE OF REDUCING REAGENTS

Proposed Mechanisms

Three general modes of decomposition of diazonium salts have been recognized and discussed by Waters.[2] These modes of decomposition may be classified according to the following descriptions of the reaction pathways: heterolytic cleavage of the carbon-nitrogen bond to give the intermediate aryl cation, homolytic cleavage of diazocompounds to give two neutral radicals (either the phenyl radical and nitrogen or the phenylazo radical) and an initial one-electron transfer reaction to give the phenylazo radical which can decompose to the phenyl radical and nitrogen. The characteristics of the reaction medium determine which one or combination of the above possibilities the diazonium salt uses in its decomposition. All of our experiments were performed in aqueous, neutral or acidic, pH 5.0 solutions, and, therefore, the phenyl cation pathway should be the predominant one.

The formation of an intermediate phenyl cation has been regarded for many years as the first and rate-determining step in the solvolysis of diazonium salts in an acidic, aqueous solution. The experimental evidence for this reaction pathway has been summarized by Lewis,[67]

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[67]E. S. Lewis, J. Am. Chem. Soc., 80, 1371 (1958).

Zollinger[3] and Brower.[68] This unimolecular pathway is supported by the observations that first-order kinetics with respect to the diazonium salt are observed, that the rate constants are independent of the anions present in solution, of the acidity over a wide range and of the solvent used, that the effect of the substituents on the aromatic ring is consistent with the unimolecular reaction but is not consistent with a bimolecular attack by the solvent, that the ratio of the chlorobenzene to the phenol produced when substituted benzenediazonium salts are decomposed in the presence of the chloride ion agrees with the unimolecular pathway, that studies of the effect of hydrostatic pressure on the rates show large, positive changes in the volume of activation and that the product ratio for the decomposition of the 4-nitrobenzenediazonium salt in the presence of the bromide ion is insensitive to changes in the pressure.

The phenyl-cation pathway has been recently modified by Lewis[69] and by Taft.[64,65,66] Lewis suggested that one of two possible reactive intermediates is reversibly formed before the loss of nitrogen. The structures of the two speculative intermediates were a spirocyclic structure and an excited state, probably vibrational, of the diazonium ion. Taft suggested that the transition state which yields the phenyl cation has a high degree of triplet radical-cation character.

The experimental evidence given by Lewis in support of his intermediates included the isotopic rearrangement of the unsubstituted

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[68]K. R. Brower, J. Am. Chem. Soc., 82, 862 (1960).

[69]E. S. Lewis and J. M. Insole, J. Am. Chem. Soc., 86, 32, 34 (1964).

and the 4-methylbenzenediazonium $-\alpha-N^{15}$ salts which accompanies their hydrolysis[69] and the small increase in the rate which is observed when the thiocyanate ion is added to the solution of the benzenediazonium salt.[70] Lewis pointed out in support of his modified mechanism that other workers have also observed a rate enhancement.[67,70] The examples given included the decomposition of benzenediazonium chloride in high concentrations, the decomposition of this salt in the presence of high concentrations of hydrochloric acid[71,72] or in the presence of thiocyanate ion, and the decomposition of the 4-nitrobenzenediazonium salt in the presence of the bromide ion.

The experimental evidence given by Taft in support of his diradical cation intermediate was based on the enhanced rate of decomposition for some meta-substituted diazonium salts. This enhancement can be detected by the Hammett correlations of the rates for the aqueous, thermal decomposition of some benzenediazonium salts. Taft[66] has shown that for several reaction series the effects of uncharged meta- and para-substituents on the reactivities of benzene derivatives may be treated as the sum of the inductive and the resonance parameters. These two effects may be separated, since meta-substituents are not affected by direct resonance interactions with the reaction center for many reactions of his series. However,

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[70]E. S. Lewis and J. E. Cooper, J. Am. Chem. Soc., 84, 3847 (1962).

[71]M. L. Crossley, R. H. Kienle and C. H. Benbrook, J. Am. Chem. Soc., 62, 1400 (1940).

[72]E. A. Moelwyn-Hughes and P. Johnson, Trans. Faraday Soc., 36, 948 (1940).

to account for the rate enhancement which is observed for some meta-substituents with the thermal decomposition of some diazonium salts, Taft[64,65] has suggested that the intermediate phenyl cation should be regarded as a triplet-state phenyl cation. This diradical is formed when a pi electron of the benzene ring falls with concerted uncoupling into the open sp^2 orbital of the cation, that is, the orbital used originally to form the carbon-nitrogen sigma bond of the diazonium salt. This electronic rearrangement is said to allow the meta-substituent to help stabilize the transition state and the intermediate phenyl cation by resonance and thereby decrease the free energy of activation. His estimates of this quantity indicated a high degree of radical-cation character for the transition state.

However, the simple phenyl cation pathway and the modifications which have been suggested by Lewis and Taft cannot account for all of the experimental results which have been reported in the literature. Some other experimental results which must be considered include non-reproducible rates, the formation of the products by erratic behavior and in nonreproducible yields, and the sensitivity of the rates towards the presence of other compounds. Some examples of these experimental results will be discussed in detail.

Crossely, Kienle and Benbrook[71] have conducted extensive kinetic and product investigations of several diazonium salts in aqueous hydrochloric acid (pH 1.95) solutions. While some of their results support the simple, phenyl cation pathway, some of their other observations showed that other considerations are also important. A slight increase in the rate was observed with increasing concentration of the hydrochloric

acid until a maximum was obtained at 10 N. The yield of the phenol decreased from 95 per cent in dilute solution to 24 per cent in very concentrated solution, while the rate increased by 13 per cent with the same change in the concentrations.

Other workers have also confirmed these observations when benzenediazonium chloride is decomposed in concentrated hydrochloric acid solution.[72] Moelwyn-Hughes and Johnson observed a 15 per cent increase in the rate in concentrated hydrochloric acid solutions or in concentrated phenol solutions but did not observe a similar rate enhancement when sodium chloride was added to the solution. They concluded that their observations were consistent with the changes in the ionic environment of the diazonium salt and offered no evidence for or against a free radical mechanism. However, if the reaction medium is irradiated, then the presence of the phenol is believed to be important.[10] The electron spin resonance spectrum of the 4-dimethylaminophenoxy radical is observed with photolysis of an aqueous solution of the corresponding diazonium salt.

If the diazonium salts are activated by a strong electron-withdrawing function, their reactions are very sensitive to the medium and particularly to other compounds present. The 4-nitrobenzenediazonium salt reacts in an acidic, sodium bromide solution to give a mixture of 4-nitrobromobenzene, 4-nitrophenol and tar.[73] Lewis and Hinds showed that the rate increased with increasing bromide concentration and that the rates were very erratic. This behavior was traced to the presence of copper

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[73]E. S. Lewis and W. H. Hinds, J. Am. Chem. Soc., 74, 304 (1952).

in the solution. A solution with added cupric sulfate decomposed at a rate too fast to measure. This sensitivity is greatly increased when the nitro function is replaced by the diazonium function. The decomposition of 4-phenylenetetrazonium ion in an acidic, aqueous, iodide solution is believed to proceed by a free radical pathway to give a variety of products, depending on the concentrations of the reactants.[9]

This remarkable sensitivity to the presence of other compounds is greatly reduced with the less activated diazonium salts. However, irregularities have also been observed for the reaction between the benzenediazonium ion and the thiocyanate ion in an aqueous solution.[70] The rate constants were erratic, and yields of products were not reproducible. The rate did show a slight increase with increasing concentration of the thiocyanate ion, and, while this increase in the rate could be caused by the reversible formation of a reactive intermediate, Cooper[74] has suggested that a free-radical process could account for this behavior and may be even more important with substituted benzenediazonium salts. In general, the less activated diazonium salts are unaffected by the presence of the cupric ion,[75] but the significance of this observation is dubious, since cuprous ion has been shown to be the effective catalyst in most copper-catalyzed reactions of diazonium salts. The chief side reaction seems to be the coupling of the diazonium salt with the phenol produced by solvolysis of the diazonium salt.[76]

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[74]J. E. Cooper, Thesis, The Rice Institute, 1959; E. S. Lewis and H. Suhr, J. Am. Chem. Soc., 82, 862 (1960).

[75]E. S. Lewis and E. B. Miller, J. Am. Chem. Soc., 75, 429 (1953).

[76]E. S. Lewis, J. L. Kinsey and R. R. Jonson, J. Am. Chem. Soc., 78, 4294 (1956).

The effects of oxygen and of the acetate ion were very pronounced in some of our experiments. Except for the 4-phenylenetetrazonium ion in the presence of the iodide ion,[9] the oxygen is believed to have little or no effect on the decomposition of diazonium salts in aqueous, acidic solutions. This behavior is the opposite to that observed when the benzenediazonium ion is decomposed in methanol using an acetate buffer.[24] When oxygen is present, only 30 to 75 per cent of the diazonium salt can be accounted for in the products, and the reaction mixture becomes a dark brown. In the absence of oxygen, 98 per cent of the reactant can be accounted for, and the solution is colorless. A complex radical-chain process involving a homolytic cleavage of the carbon-nitrogen bond of the intermediate diazo compound was proposed to account for these results.

There is little evidence in the literature concerning the possible effects of the acetate ion in aqueous, acidic solutions, although the decomposition of N-nitrosoacetanilides and diazonium salts in basic, acetate solutions are known to involve a free radical pathway.[40] DeTar[24] has attempted to extract benzenediazoacetate with toluene from an aqueous solution containing acetate ions and benzenediazonium ions. He estimated the equilibrium constant for the formation of the diazo compound to be less than 10^{-5} $mole^{-1}l.$ when he could not isolate any benzenediazoacetate. This small equilibrium constant was said to agree with the ultraviolet spectra studies of Lewis which were reported by DeTar by private communication.

Reactivities

Our discussions of the experimental results which have been reported in the literature have emphasized that diazonium salts can react by

several different pathways. The choice of the pathway or combination of pathways by the diazonium salt depends on the substituent groups and the reaction conditions.

The importance of the characteristics of the diazonium salts can be explained in terms of resonance and inductive interactions between the diazonium function and the other substituents. The magnitudes and the influences of these possible interactions are indicated by both theoretical and experimental considerations.

Schuster and Polansky[77] have examined the pi electron structure of several organic diazo compounds by carrying out theoretical calculations. The three diazonium ions which they considered were the unsubstituted and the 4-substituted nitro- and N,N-dimethylaminobenzenediazonium ions. The quantities they calculated for these three diazonium ions included the bond order of the carbon-nitrogen bond; the pi electron energy of the phenyl cation, of the diazonium group, $-N_2^{(+)}$, and of the benzenediazonium ion, $Ar-N_2^{(+)}$; and the enthalpy for the decomposition of the diazonium salt to a phenyl cation and nitrogen. The order of increasing stability of the ground states was $O_2N->H->(CH_3)_2N-$ for the three diazonium salts according to the calculations for the bond-order and enthalpy for the decomposition of the diazonium salts. The calculations for the pi electron energy of the phenyl cation and of the benzenediazonium ion indicated that both of these species possessed the same order of increasing stability, that is $O_2N->(CH_3)_2N->H-$.

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[77]P. Schuster and O. E. Polansky, Monatshefte für Chemie, 96, 396 (1965).

The experimental methods which have been employed to relate the structure and the reactivity of the diazonium ions include spectra studies, kinetic studies and Hammett correlations.

Nujol mulls have been used to record the infrared spectra of several diazonium salts.[78] The characteristic absorption of the diazonium group in 4-6 μ region was dependent on the substituent functions of the aromatic nuclei and very slightly dependent on the anion. This characteristic absorption disappeared when the triazene derivatives were made from the diazonium salts. Other workers have discovered that systematic, linear relationships exist between these infrared nitrogen-nitrogen bond stretching frequencies and the Hammett substituent sigma$^+$ constants as well as for the rate constants for the coupling reactions of 6-naphthol-2-sulfonate with the diazonium salts.[79] These studies confirm that strong resonance interaction in the expected sense occurs in the ground state of diazonium salts between the diazonium function and the para substituents.

Visible and ultraviolet absorption spectra studies have also confirmed the stabilization of diazonium salts by electron-donating groups.[80] Substituents in the para position can stabilize the diazonium group by direct conjugation between the two functions. This interaction, which can best be described as a quinonoid structure, was indicated to be im-

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[78]K. B. Whetsel, G. F. Hawkins and F. E. Johnson, J. Am. Chem. Soc., 78, 3360 (1956).

[79]R. J. Cox and J. Kumamoto, J. Org. Chem., 30, 4254 (1965).

[80]L. C. Anderson and J. W. Steedly, Jr., J. Am. Chem. Soc., 76, 5144 (1954).

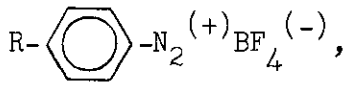
portant in the 4-N,N-dimethylaminobenzenediazonium chloride by noting the similarities of the spectra of this diazonium salt and diphenylquinomethane.

The results of the kinetic studies and Hammett correlations which are reported in Table 1 also show this same general trend. Crossely, Kienle and Benbrook[71] have determined the Arrhenius equation parameters for the thermally induced decompositions of a number of diazonium ions in acidic, aqueous solutions. The rate constants for the diazonium salts which were used in our studies have been calculated from these parameters for the temperature which was used in our experiments, that is, 30.0° C. The two sigma quantities which are also given in Table 1 have been defined by Taft[64,65,66] as the resonance effect of each substituent in the para, (σ_R^p), and meta, (σ_R^m), positions. These quantities are specific for the thermally induced decomposition of diazonium salts in acidic, aqueous solutions. The sign and magnitude of these quantities support both the suggested diradical phenyl cation intermediate as well as the classical notion of resonance stabilization. The classical notion is that the ground state but not the transition state is stabilized by electron-releasing groups in the para position by direct resonance interaction of the two functions and that, therefore, their rate of decomposition is decreased. Taft[66] has discussed at great length the idea that these direct resonance interactions with meta substituents are impossible in the ground state but that the increase in the rate of decomposition for these meta substituted diazonium salts can be explained by the stabilization of the transition state by the diradical phenyl cation. The last column gives his estimates for the decrease in the free energy of

Table 1

Quantities Indicating Stabilities of Diazonium Salts

Diazonium Salts,



where R- is,	Rate Constants, $sec.^{-1}$	Sigma Constants σ_R^p	σ_R^m	Decrease in the free energy of activation, kcal./mole.
CH_3O-	1.4×10^{-3}	+0.62	-0.44	1.7
CH_3-	1.0×10^{-5}	+0.27	-0.11	0.5
Cl-	---------	+0.27	-0.14	0.2
H-	6.1×10^{-5}	-----	-----	---
O_2N-	2.1×10^{-5}	-0.06	-0.09	---

activation due to this stabilization.

The reaction medium can influence the choice of the reaction pathway by the polarity of the solvent, the pH of the solvent, the presence of other compounds which could act as a reductant or a free radical chain initiator, the presence of free radical trapping agents, and the presence of anions which can enter into an equilibrium with the diazonium salt to form a diazocompound. The literature evidence concerning the influence of all of these factors except for the presence of anions in solution has already been discussed extensively. The important influences that the anions in solution can exert are that they can effectively reduce the concentration of the diazonium ion as well as lead to the initiation or termination of free radical reactions.

The equilibrium between the diazonium salts and a variety of anions has been reviewed by Zollinger.[3] These equilibria represent reactions where the terminal nitrogen of the diazonium function acts as a Lewis acid to accept a pair of electrons from the anion. The resulting compound is a reasonably stable azo compound. These reactions are related to the coupling reactions where diazonium salts are reacted with activated aromatic amines and phenols. In these latter cases the reaction is rendered irreversible by the loss of a proton.

Examples of equilibria between diazonium salts and various anions include the studies with the hydroxide, the sulfite and the cyanide anion to form the syn-diazotate, the syn-diazosulfonate and the syn-diazocyanide, respectively.[81] The Hammett rho values for all of these equilibria as

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[81]E. S. Lewis and H. Suhr, Chem. Ber., 92, 3043 (1959).

well as for the coupling reactions with aromatic amines and phenols are very high, ranging from 3.85 to 6.3. These reactions are complicated by the formation of the two possible stereoisomers about the nitrogen-nitrogen bond as well as the decomposition of the diazonium salt to the phenol.

The experimental technique used to study these equilibria was to record the spectra of the separate solutions as well as mixtures of the two reactants. The workers observed large shifts in the position of the absorption peaks and also changes in the extinction coefficients. These new peaks were attributed to the diazo compounds.

CHAPTER IV

PURPOSE OF THE RESEARCH WORK PRESENTED IN THIS THESIS

In the discussion presented in the first three chapters of this thesis, preliminary experimental results and references from the chemical literature were cited which indicated that the reactions and their pathways of diazonium salts are not nearly as simple and independent of the reaction medium as they are generally believed to be. We have, therefore, performed certain experiments designed to help to clarify the nature of some of these reactions.

The original approach for this investigation consisted of studying the kinetics of the reaction between TMPD and the different diazonium salts according to Eq. 8. This was accomplished experimentally by following the increase in the absorption at 610 mμ. This absorption is caused by the formation of the radical cation of TMPD. The rate constants for the decomposition of the diazonium salts in the absence of the TMPD were also determined under as nearly identical experimental conditions as it was possible to duplicate, so that direct comparisons of these reactions could be made.

As the work progressed for the study of this reaction, it quickly became apparent that much time and effort would have to be devoted to the design of the experimental apparatus and procedure due to the sensitivity of this reaction to the exact reaction medium. Besides attempting to refine these important factors, other systems and experimental

procedures were sought which would not be as sensitive to the reaction medium. This search led to the use of other compounds with higher oxidation potentials which could serve as complexing or one-electron transfer reagents. The reduced reactivity and sensitivity of these new systems allowed other experimental techniques to be used. For example, solutions of the diazonium salt and the potential complexing reagent as well as a solution containing both reagents could be carefully made up and their ultraviolet and nuclear magnetic resonance spectra carefully recorded. Comparison of these spectra in some cases revealed differences which could not be attributed to either compound alone and which were, therefore, evidence for a complex formation between the two reactants.

However, before these new experiments were performed, a new synthetic reaction sequence was investigated for the preparation of TMPD and other related tertiary aromatic amines. The compounds obtained from this sequence, as well as several commercially prepared compounds, were used in both our kinetic studies and in our studies seeking evidence for complex formation.

The results of this research effort have led to the investigation of a new analytical approach for following the decomposition of diazonium salts, to the investigation of several new reaction sequences, to the refinement of a well established reaction, and to a better understanding of the possibilities of one-electron transfer reactions and complex formations involving diazonium salts.

CHAPTER V

EXPERIMENTAL INSTRUMENTS, PREPARATION OF REAGENTS, EXPERIMENTAL APPARATUS AND PROCEDURE

Instruments Used

The ultraviolet and visible spectra were recorded with the use of three instruments. When the research effort was begun, a single-beam Beckmann Model DU spectrophotometer was used for the kinetic studies. This instrument was replaced by a Zeiss Model PMQ-II single-beam spectrophotometer. A double-beam Cary Model 14 recording spectrophotometer was used to record the final spectra of the reaction solutions as well as for the studies seeking evidence for complex formation.

A bath, maintained at constant temperature ($\pm 0.01^{\circ}$ C) and filled with ehtylene glycol, was placed beside the Zeiss spectrophotometer. A Beckmann differential thermometer, which had been calibrated with a National Bureau of Standards thermometer, was permanently placed in the bath to maintain a check on the temperature. During the kinetic studies, the quartz cell was placed in the constant temperature bath. This cell could be quickly and easily removed from the bath and placed in the Zeiss spectrophotometer to record the absorption due to one of the reactants.

The nuclear magnetic resonance spectra used in the studies to find evidence of complex formation, to check the purity of the reactants and for the identification of the products were all recorded with the aid of a Varian A-60 instrument.

The melting points were taken in glass capillary tubes placed in an

oil bath. Uncorrected Anschutz thermometers obtained from the Brooklyn Thermometer Company were used to determine the temperature of the bath.

Preparation of the Diazonium Salts

As the work for this thesis progressed, a continuous effort was made to eliminate the impurities present in the diazotization process, although the basic reaction between the aniline and n-butylnitrite was kept unchanged. Improvements in the method include the purification of the aromatic amines, of the diazotization reagent, and of the solvents used.

The 4-nitroaniline was purified by recrystallization from hot water, aniline was purified by distillation, and 4-methoxyaniline, 4-methylaniline, 4-chloroaniline, 4-bromoaniline and 4-iodoaniline were purified by sublimation. Their purity was confirmed by comparing their melting points with the literature values and by recording their nuclear magnetic resonance spectra (Table 17). The n-butylnitrite, prepared in the usual manner,[82] was purified by distillation and stored over calcium chloride. The solvents were purified by distillation. Stock acetone was distilled from phosphorus pentoxide and the diethyl ether was predried over calcium hydride and then distilled from a lithium aluminum hydride solution within 18 hours before use. The 40 to 50 per cent fluoroboric acid in aqueous solution, Baker Analyzed Grade, was used without additional purification.

Except for aniline, all of the aromatic amines, 0.10 mole, were dissolved in 25 ml. of acetone and a 50 per cent molar excess, 0.15 mole,

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[82]W. A. Noyes, "Organic Synthesis," vol. II, p. 108, New York (1943).

of the aqueous fluoroboric acid solution. To this solution, which was placed in an ice-bath, n-butylnitrite, 0.15 mole, was added dropwise, with vigorous shaking. After an additional 15 minutes, precipitation was caused by the addition of 200 ml. of diethyl ether. The diazonium salt was collected by filtration and washed with an additional 200 ml. of diethyl ether. After the diazonium salt had been recrystallized twice by dissolving it in acetone and then precipitating and washing it with diethyl ether, it was dried in vacuum for two hours.

Anilinium fluoroborate was made by dissolving the freshly distilled aniline in a 50 per cent molar excess of 50 per cent fluoroboric acid solution. The salt, which crystallized from solution, was filtered and dried under vacuum for six hours. The fluoroborate salts of 4-anisidine and p-toluidine did not crystallize when the amines were similarly treated, presumably due to their greater solubility in water. The purity of the anilinium salt was confirmed by titration with standardized sodium hydroxide solution. In the preparation of benzenediazonium fluoroborate, the fluoroboric acid solution was deleted.

Preparation of One-Electron Transfer Reagents

When work was begun for this thesis, a satisfactory synthesis for the one-electron transfer reagent TMPD was not known. The usual method employed for its preparation was the N-methylation of p-phenylenediamine by heating its dihydrochloride with methanol in a sealed tube.[83] The new method discovered by us for the preparation of TMPD involves an initial reaction of chloro- or iodoacetic acid with the diamine to yield

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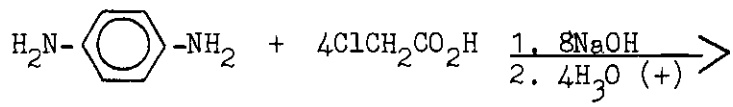
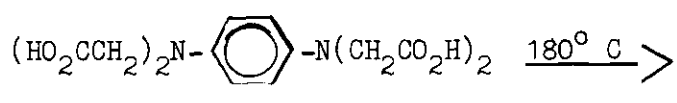
[83]R. Meyer, Chem. Ber., 36, 2979 (1903).

4-phenylenediiminotetraacetic acid. This intermediate product was then decarboxylated to the desired TMPD by heating the dry solid in a large vacuum sublimation apparatus.[84] The reaction sequence is illustrated by Eqs. 13 and 14.



$$H_2N\text{-}C_6H_4\text{-}NH_2 + 4ClCH_2CO_2H \xrightarrow[2.\ 4H_3O\ (+)]{1.\ 8NaOH} (HO_2CCH_2)_2N\text{-}C_6H_4\text{-}N(CH_2CO_2H)_2 \quad \text{(Eq. 13)}$$



$$(HO_2CCH_2)_2N\text{-}C_6H_4\text{-}N(CH_2CO_2H)_2 \xrightarrow{180^\circ\ C} 4CO_2 + (H_3C)_2N\text{-}C_6H_4\text{-}N(CH_3)_2 \quad \text{(Eq. 14)}$$

The first experimental procedure for performing reactions according to Eq. 9 was to add all of the reactants in a round-bottomed flask and reflux in the concentrated basic aqueous sodium hydroxide solution. We found that a more satisfactory yield could be obtained by carrying out the reaction under milder basic conditions. The improvements included the replacement of sodium hydroxide with sodium bicarbonate and the addition of the sodium salt of 2-haloaliphatic acid aqueous solution dropwise with a dropping funnel. The decarboxylation must be carried out under a pressure of approximately 20 mm. of Hg, and the pressure must be obtained with a water aspirator and not at a lower pressure such as that obtained from an unregulated, mechanical vacuum pump.

The general reaction procedure for methylation of aromatic monoamines

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[84] J. R. Cox, Jr. and B. D. Smith, J. Org. Chem., 29, 488 (1964).

was to add 0.10 mole of the amine to 100 ml. of water which was heated to boiling under reflux in a three-necked, round-bottomed flask. To this heterogeneous mixture, a solution of 0.25 mole of the chloracetic acid and 0.40 mole of sodium bicarbonate in 100 ml. of water was added dropwise with a dropping funnel. The solution was boiled under reflux for an additional hour and then allowed to cool to room temperature. Addition of 20 ml. of concentrated hydrochloric acid to the solution yielded the iminodiacetic acid as a precipitate. The reaction procedure for the aromatic diamines was the same as the procedure described for the monoamines, except that the molar quantities of the aliphatic acid, sodium bicarbonate and concentrated hydrochloric acid were doubled.

When the 2-chloropropanoic acid was used, the acid failed to precipitate when isolation was attempted by the above procedure. The sodium salt of the imino acid was collected as a solid by cooling the reaction mixture. Concentrated hydrochloric acid was then added directly to this solid. The salt mixture slowly dissolved, whereupon the acid crystallized from the solution and was collected by filtration.

The solid imino acids prepared by the above procedures from chloroacetic acid and 2-chloropropanoic acid were decarboxylated according to the procedure described by Eq. 10. The solid acid was placed in the bottom of a large vacuum sublimation apparatus and heated to a temperature approximately 25° C above its melting point. The apparatus was evacuated before and during the decarboxylation with a water aspirator. The product was collected on the cold finger of the apparatus. When the product was a liquid or a solid melting close to room temperature, a special sublimation apparatus was used, the cold finger of which was

cooled by means of dry ice and acetone placed directly in the cold finger, rather than the usual procedure of running tap water through the cold-finger.

These potential one-electron transfer reagents were purified by dissolving the amine in petroleum ether (b.p. 36-60° C) and passing this solution through a short column of basic activated alumina. After evaporation of the solvent, the amine was further purified by vacuum sublimation. All of the amines, except TMPD, were used directly as the pure compound.

The amine TMPD is stable in contact with air, but with light and moisture excluded, for extended periods of time. However, under the experimental conditions which we used for TMPD, we felt it necessary to make the difluoroboric acid salt of TMPD to insure its purity. This acid salt was prepared by dissolving the tertiary amine in a 50 per cent molar excess of fluoroboric acid solution and then collecting the precipitated acid salt by filtration. The excess acid was removed by placing the acid salt under vacuum, approximately 1.0 mm. of Hg, in a desiccator for one week. The purity of this acid salt was confirmed by calculating the molecular weight from the two equivalent points found by titrating a known weight of the acid salt with standardized sodium hydroxide solution.

The preparation of 4-nitrodimethylaniline could not be achieved by the above procedure because of the deactivating influence of the nitro group towards alkylation. Therefore, the procedure of Campbell was used to prepare this potential one-electron transfer reagent.[85] A solution

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[85]T. W. Campbell, J. Am. Chem. Soc., 71, 740 (1940).

containing 0.37 mole of dimethylamine hydrochloride in 10 ml. of warm water was added to a mixture of 0.21 mole of 4-nitrobromobenzene in 300 ml. of pyridine and 0.60 mole of sodium bicarbonate. This reaction mixture was boiled under reflux for 10 hours. The hot solution was then filtered and the solid removed by filtration and then extracted with 200 ml. of acetone. This acetone extract was added to the filtrate, which was then heated to boiling. To this hot solution, water was added slowly until the solution became cloudy. Cooling the solution to room temperature yielded the yellow needles of p-nitromethylaniline in 95 per cent yield. After recrystallization from methanol, the melting point of the product was 163.5-164.0° C. However, when we substituted diethylamine for the dimethylamine, we recovered the starting material unchanged, as indicated by its melting point. This was probably due to the poor quality of our sample of diethylamine.

Several of the tertiary amines prepared by these experimental procedures, together with several other commercially prepared compounds, have been used in both our kinetic and complex formation studies.

Preparation of Solvents, Buffers and Nitrogen

The first kinetic studies were performed with water from the metallic still of the chemistry department. With the increasing awareness of the sensitivity of the reaction between TMPD and the various diazonium salts to trace amounts of extraneous materials, considerable effort was made to remove the last trace amounts of both organic and inorganic materials, particularly molecular oxygen, from the reaction vessel and medium. This section is concerned with developments in removing extraneous materials from the solvents, nitrogen and buffer stock solutions. The

following section relates a similar progression of events for the apparatus and the experimental procedure.

The first reaction solutions were made with water from the metallic still, which had been deoxygenated by heating the water to boiling for thirty minutes. No effort was made to purify the water, and neither was there any effort to remove trace amounts of extraneous materials from the preparative or reaction vessels at this time, other than to wash the vessels with soap and water.

In an attempt to remove more oxygen from the reaction medium, a series of apparatuses was developed in which the solvents could be deoxygenated by a freezing-thawing process under vacuum. In the final stages of the development of these apparatuses, a special all-glass still was also constructed in which the solvent could be distilled in a nitrogen atmosphere. This still was designed to purify the solvent by distillation and to assist in the deoxygenation of the solvent by saturating it with nitrogen.

Approximately one liter of water from the metallic still was placed in the two-liter, round-bottomed flask which composed the bottom portion of the still. To this water, approximately 5 gr. of potassium permanganate and 2 gr. of sodium hydroxide were added. Nitrogen was bubbled through this solution and then allowed to sweep out the remainder of the apparatus. Thus the solvent was distilled under an atmosphere of nitrogen into the reservoir on the still. From this reservoir, a known, constant volume of approximately 50 ml. was delivered directly into the reaction vessel.

The nitrogen used in this distilling process was commercially prepurified. It was then passed through two gas wash bottles containing a

chromous sulfate solution and then through one gas wash bottle containing concentrated sulfuric acid. The chromous sulfate solution used to remove the last trace amounts of oxygen from the prepurified nitrogen was prepared by dissolving 50 gr. of the chromic salt, $CrK(SO_4)\cdot 12\ H_2O$, and 27 ml. of concentrated sulfuric acid in two liters of water. This blue-green solution was poured into the gas wash bottles together with approximately 5 gr. of zinc. Nitrogen was bubbled through the solution until it became a deep blue; this color change indicated that the solution was ready for use.

The stock buffer solutions were prepared with water from the still described above. All of the reagents used in the buffer solutions were Baker Analyzed Grade. The early work used potassium acid phthalate as the buffer, but it was replaced by phosphate-phosphoric acid and acetate-acetic acid buffers. This substitution was necessary because of the strong absorption of the potassium acid phthalate in the ultraviolet region. The sodium acetate, with three moles of water of crystallization, was used directly without recrystallization, after being dried under vacuum, 10 mm. of Hg, and heated to 80° C. The liquid reagent grade acetic and phosphoric acids were used directly. These stock buffer solutions, usually 5 ml., were added by means of a pipette to the reaction vessel, together with additional solvent from the still, to make up the reaction medium.

Apparatus and Experimental Procedure Used to Collect Data for Kinetic Studies

All of the kinetic studies performed for this thesis used the change in the absorption maximum of the reactants in the ultraviolet and visible regions as the analytical means for following the progress of the reaction.

The concentrations of the reactants are directly proportional to their absorption at their absorption maximum according to the relationship which is known as Lambert-Beer's Law. This is stated in its mathematical form by Eq. 15, where "A" is the absorption, "e" is the molar extinction coefficient, "l" is the length of the light path through the reaction solution in the cell, and "c" is the concentration of the reactant.

$$A = e\,l\,c, \text{ where } A = -\log\left(\frac{\text{Transmitted Radiation}}{\text{Incident Radiation}}\right) \qquad \text{(Eq. 15)}$$

The studies presented here are those in which the diazonium salt is allowed to decompose in the presence and absence of a one-electron transfer reagent. The experimental conditions in these two cases are duplicated as nearly as possible so that comparisons of the two reactions can be made. A limited number of studies were performed in an attempt to determine the effect of other compounds, such as oxygen, hydrogen peroxide and the acetate anion.

As the research effort progressed, it became increasingly apparent that these reactions of the diazonium salt were extremely sensitive to trace amounts of extraneous compounds, as well as to the experimental conditions. This sensitivity was increased by the use of low concentrations, 10^{-4} to 10^{-5} molar, of the reactants. Therefore, the accuracy of our studies was limited by our ability to remove these extraneous compounds, by our ability to prepare the reactants, by our ability to remove impurities from the reaction medium, by the limitation of the spectrophotometer in determining the absorption accurately, and by our ability to calculate the rate constants. Because of the difficulty in determining the importance of, and in controlling, these factors, much

time and effort had to be spent in designing the apparatus and an experimental procedure which would give the best possible results.

The first experiments were performed by making up the buffered solutions of the TMPD and the diazonium salt with water from the metallic still, which was heated to boiling for thirty minutes in an attempt to deoxygenate the water. The reaction was then initiated by mixing equal volumes of these two solutions. This reaction solution was then placed in an ordinary open-top, 1 cm., Beckmann quartz cell, and a Beckmann DU spectrophotometer was used to determine the absorption at this stage. This method allowed oxygen to be slowly absorbed from the atmosphere. Therefore, a closed apparatus was adapted in hope of obtaining more reproducible and meaningful results by eliminating this unpredictable reaction factor. For purposes of giving the experimental data later, this procedure is labelled Procedure I.

The apparatus shown by Figure 1 was then designed and used in the following manner. The reactant solutions were again made with water which had been heated to boiling for thirty minutes. Five ml. of the two buffered solutions containing the reactants were placed in each arm of the apparatus. The solutions were degassed by freezing them in an ice-salt bath and then evacuating the apparatus to approximately 10 mm. of Hg. The solids were then allowed to thaw under their own vapor pressures. After repeating this freezing-thawing process three times, the two solutions were mixed and the change in the absorption maximum recorded. This is labelled Procedure II.

Freezing of the solutions frequently broke the quartz cell, and thus an additional and larger container was added to the side opposite

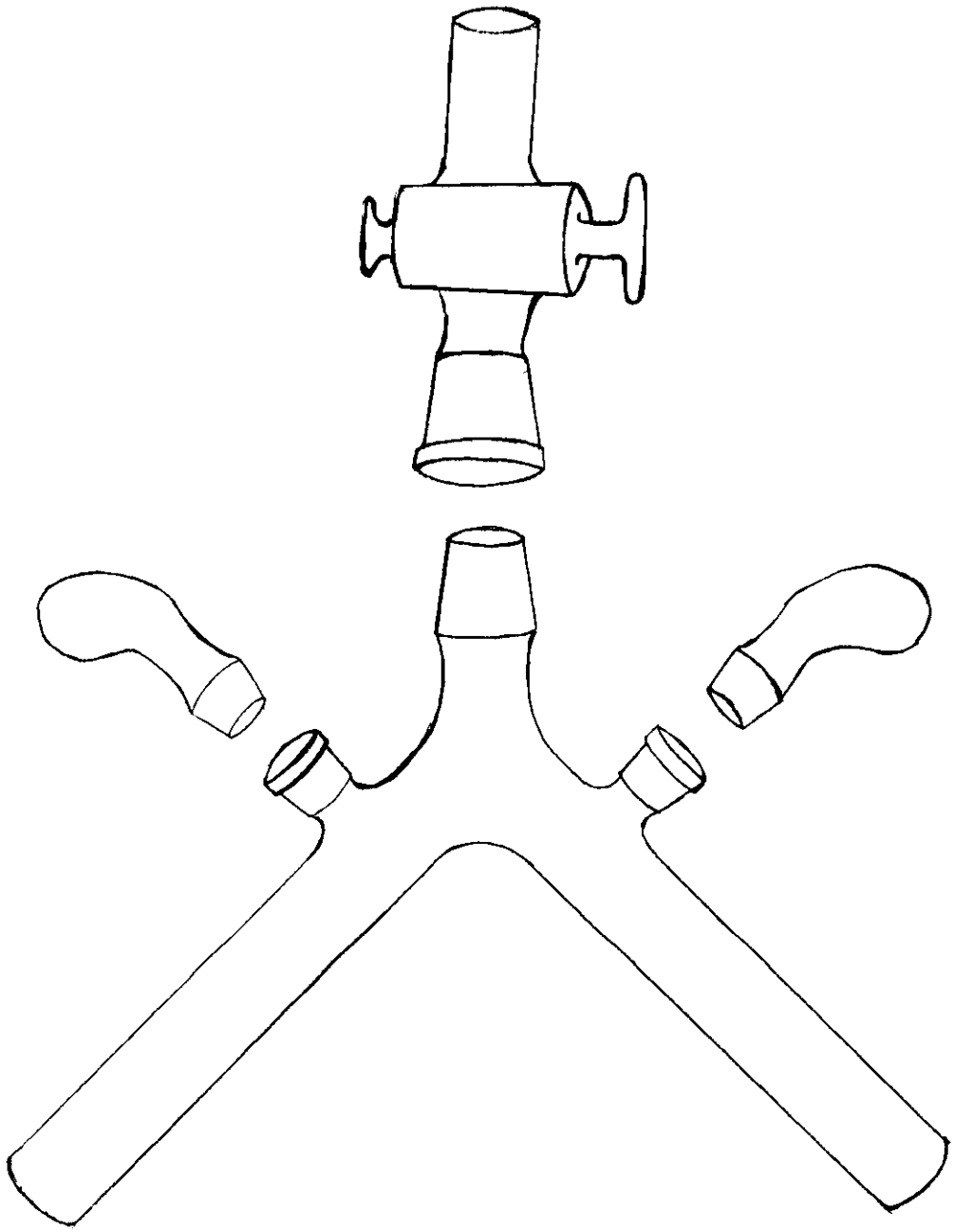

Figure 1. First Degassing Apparatus

the quartz cell. Together with the already present and enlarged container, 10 ml. of each solution containing the two reactants could be added to the apparatus and then the solutions degassed and the progress of the reaction followed as before. This method permitted the decomposition of the diazonium salt during the degassing procedure and allowed the oxygen present in the apparatus to react with the TMPD solution before the reaction between the diazonium salt and the TMPD was initiated. Therefore, the method was again modified as described below.

The use of an apparatus similar to that shown in Fugure 2 was then initiated. The first apparatus of this general design did not have a stopcock immediately below the quartz cell and the apparatus was connected to an ordinary mechanical vacuum pump system by means of rubber tubing. The buffer solution, approximately 50 ml., was placed in the bottom portion and degassed by the freezing-thawing method. The two solid reactants were weighed in small glass-weighing cups and placed in the side arms. This is labelled Procedure III. After the final thawing of the ice, the vapor pressure of the reaction medium determined the internal pressure of the apparatus. The curves, obtained by plotting $\ln(A_{INF}-A_T)$ versus the time, were shaped like the letters "S" and "Z." This behavior could possibly be explained by the fact that the apparatus allowed air to leak slowly into the apparatus so as to finally equalize the internal and external pressures and the sensitivity of the reaction to oxygen. Thus the apparatus and procedure were again modified. All of the kinetic rate constants which are reported in this thesis used the apparatus and procedure described in the following paragraphs. The plotting of $\ln(A_{INF}-A_T)$ versus the time gave a straight line over several half-lives, with the

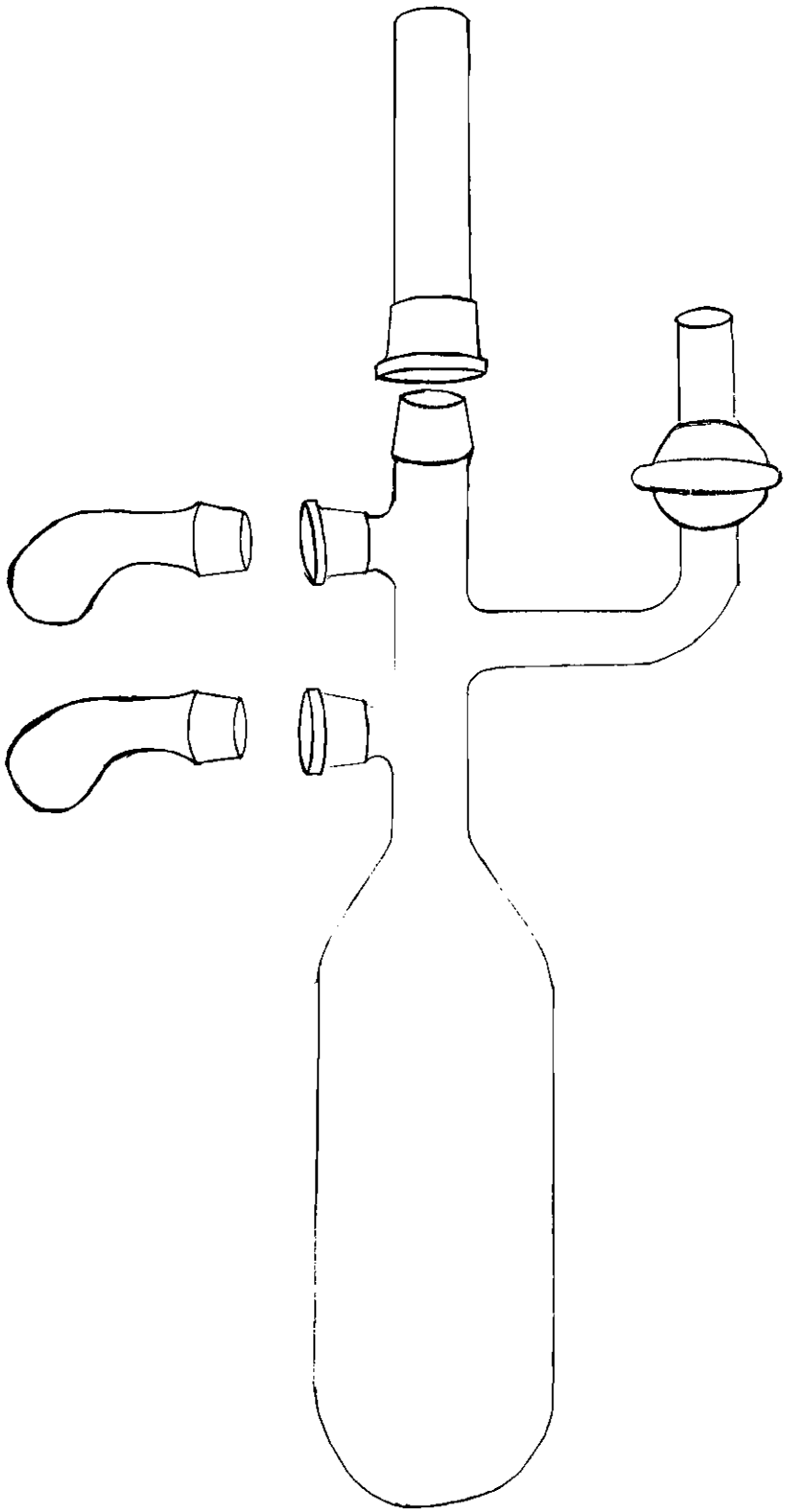

Figure 2. Second Degassing Apparatus

modifications to be described here.

The precautions already described in the preceding sections were initiated to insure the purity of the solvents, buffers and reactants.

A ground glass joint was added so that the apparatus could be connected directly to a high vacuum system. A stopcock was also added so that the quartz cell compartment could be closed off and removed. All of the ground glass joints on the apparatus were paired, labelled and polished with 800 mesh carborundum grinding powder. These joints were sealed with Apiezon high vacuum grease, Type N.

A new high vacuum system was constructed and reserved for the degassing procedure. This system used a mechanical two-stage Welch Duo-Sealed high vacuum pump capable of a maximum vacuum of 0.05 microns of Hg. This maximum vacuum could occasionally be obtained during the degassing procedure, but the usual vacuum obtained was between one and five microns. This high vacuum system allows two apparatuses to be connected at the same time to the vacuum manifold. The manifold could be closed off from the rest of the system and nitrogen introduced directly into the manifold and, thereby, into the apparatuses. The nitrogen was purified in the same manner as described in the preceding section.

An apparatus was prepared for a kinetic experiment by first removing all of the old stopcock grease with chloroform, washing with soap and water, and rinsing it with concentrated nitric acid, followed by another rinse with water from the all-glass still described in the preceding section. It was then dried in an oven set at 130° C. Freshly distilled water from the special still and buffer stock solution were added to the apparatus and the reactants placed in the side arms by means

of small glass-weighing cups. The buffer solution was frozen with the aid of a dry ice, acetone bath, with the bath temperature at approximately -70° C. The apparatus was then evacuated to the best possible vacuum. The apparatus was filled with nitrogen and again evacuated. This procedure, which was used to remove trace amounts of oxygen from the apparatus, was repeated twice. Afterwards, the apparatus was evacuated again and the solid reaction medium allowed to thaw under its own vapor pressure. The dissolved gases, which had been squeezed out of the crystal lattice, bubbled out of the solution. This freezing-thawing process was repeated four times, and the last time no bubbles were observed emerging from the crystal lattice. After the final degassing step, a vacuum was left in the quartz cell compartment, but the remainder of the apparatus was filled with nitrogen to a pressure just below that of the atmospheric pressure. The apparatus was allowed to come to thermal equilibrium in the constant temperature bath. The reactants were then mixed with the buffer solution and the quartz cell compartment filled with the reaction solution. This portion of the apparatus was sealed by means of the stopcock, and the compartment was removed. Care was taken to place the quartz cell in the Zeiss single-beam spectrophotometer used to determine the absorption at this stage in exactly the same manner each time. At the completion of the kinetic study, the complete ultraviolet and visible spectra were recorded with a Cary 14 double-beam recording spectrophotometer. These spectra were used to identify the principal product of the reaction. This is labelled Procedure IV.

The progress of the reaction was followed until there was no further change in the absorption readings at the wave length of the absorption

maximum of the reactant. This final reading was taken as the infinity value for the purposes of calculating the rate constant.

For preparative scale experiments, the same degassing procedure and an apparatus of the same general design were used, except that the quartz cell was replaced by a ground glass stopper. A 250 ml. Erlenmeyer flask was used as the reaction vessel for the kinetic studies, and no attempt was made to degas the reaction medium. The same care was taken in preparing the reactants, reaction solutions and vessel as was taken with the degassed kinetic studies for both the preparative experiments and the non-degassed kinetic studies.

Mathematical Treatment of Kinetic Data

The mathematical treatment of the rate data consisted of calculating the rate constant for each reaction studied. The decomposition of the diazonium salt was studied both in the presence and in the absence of TMPD and other potential electron-transfer reagents under as nearly the same experimental conditions as was possible, in order to duplicate the conditions. Under the experimental conditions which were used, the rate of decomposition of the diazonium salt should have been first order with respect to the diazonium salt, since it was present in limiting concentration. Thus, the rate constants were at first calculated by the generally accepted procedure of plotting the quantity $\ln(A_{INF}-A_T)$ versus the time and determining the slope of the line.[86] The first-order rate constant was then equal to the value of the slope when natural

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[86]A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, New York, Second Edition (1961).

logarithms, ln, were used. The first-order rate constants calculated by this method showed large deviations. Therefore, the decision was made to write a program for the Burroughs 5500 Computer to calculate the first-order rate constant by as many different mathematical methods as possible.

All of the computer calculations were based on the four relationships given by Eqs. 16 through 19. The two relationships of Eq. 17 and Eq. 18 could be derived directly from the simple first-order rate relationship of Eq. 16. The last relationship, of 19, was derived from Eq. 17.

The relationship given by Eq. 18 was a general equation which could be derived from Eq. 17 if there existed a linear relationship between the measured physical quantity, in our case the absorption, and the concentration of the reactant.[86] The mathematical derivation of Eq. 18 took into account the contribution of the other compounds present and the contribution of the reaction medium to the physical property being measured.

The latter two equations, Eq. 18 and Eq. 19, were obtained from Eq. 16 and Eq. 17, respectively, by substituting the numerical values for two different pairs of data points into either Eq. 16 or Eq. 17 and by subtracting the two resulting equations. In their general mathematical forms, the quantities "A", "t" and "A'", "t'" corresponded to the two different pairs of absorption and time data points used in the calculation. These equations calculated the slope, equal to the rate constant, of the line between the two pairs of data points selected. The pairs of data points which were used in the calculations were adjacent data points, alternate (every other) pair of data points, and every possible pair of data points. The use of Eq. 18 eliminated all dependence on the initial, A_{INT}, absorption values, while Eq. 19 eliminated all dependence on the

initial absorption value. The three relationships of Eq. 16, Eq. 17 and Eq. 19 were dependent on the initial, on the initial and infinity, and on the infinity absorption values, respectively. Eq. 18 was not dependent on either of these quantities. The apparent importance of their dependence on the initial and infinity absorption values is discussed in a subsequent section.

$$kT = \ln(A_{INT}/A_T) \qquad \text{(Eq. 16)}$$

$$kT = \ln(A_{INF}-A_{INT})/(A_{INF}-A_T) \qquad \text{(Eq. 17)}$$

$$k(T-T') = \ln(A'/A) \qquad \text{(Eq. 18)}$$

$$k(T-T') = \ln(A_{INF}-A')/(A_{INF}-A) \qquad \text{(Eq. 19)}$$

$$KL = \frac{\sum \ln(DIF) \times \sum(LT) - N \times \sum \ln(DIF) \times (LT)}{(\sum LT)^2 - N \times \sum(LT)^2} \qquad \text{(Eq. 20)}$$

$$BL = \frac{(\sum LT) \times (\sum \ln(DIF) \times (LT)) - \sum(LT)^2 \times \sum \ln(DIF)}{(\sum LT)^2 - N \times \sum(LT)^2} \qquad \text{(Eq. 21)}$$

$$AL = KL \times LT - BL \qquad \text{(Eq. 22)}$$

The eleven different mathematical methods of the program used the four equations numbered 16 through 19 as written and a least squares treatment of the four equations to give the best possible straight line for the data points which were given the computer. The general equations used to calculate the least squares rate constant, KL, and the least squares constant BL were given by Eq. 20 and and by Eq. 21, respectively. From the relationship between KL and BL given by Eq. 22, the absorption

value, AL, which corresponded to the value necessary to give perfect agreement with the least squares treatment, was calculated for each time that was given the computer.

The quantities, DIF and LT, which are used in Eq. 20 and Eq. 21, are mathematical variables related to the absorption and time values, respectively. The exact mathematical forms of these two variables depends on the method of calculation used, and they are given in the summary of the methods. The quantity N is the number of data points used in the calculation. The capital Greek letter sigma, $\sum$, is a mathematical symbol denoting the summation of the quantity immediately following over all of the data points. Natural logarithms, ln, are used in the calculations. A description of each method follows:

(a) Least squares treatment of Eq. 17 for each data point, DIF = $(A_{INF}-A_T)$, LT = T.

(b) Least squares treatment of Eq. 19 for pairs of adjacent points plus pairs of alternate (every other) points, DIF = $(A_{INF}-A')/(A_{INF}-A)$, LT = $(T-T')$.

(c) The average of all the rate constants calculated by Eq. 19 and using pairs of adjacent points plus pairs of alternate (every other) points.

(d) The average of all the rate constants calculated by Eq. 17 for each data point.

(e) The average of all the rate constants calculated by Eq. 16 for each data point.

(f) Least squares treatment of Eq. 16 for each data point, DIF = A_{INF}/A_T, LT = T.

(g) Least squares treatment of Eq. 18 and using every possible pair of data points, DIF = A'/A, LT = (T-T').

(h) The average of all the rate constants calculated by Eq. 18 and using every possible pair of data points.

(i) Same method as (h) except that only pairs of adjacents are used.

(j) Same method as (h) except that only every other pair of data points is used.

(k) Least squares treatment of Eq. 18 using pairs of adjacent points plus pairs of alternate (every other) points, DIF = A'/A, LT = (T-T').

These methods for calculating the rate constant can be divided into three groups according to their dependence on the initial and infinity absorption values. The first three methods depend on the infinity value only, the fourth depends on both the infinity and initial values, the fifth and sixth depend on the initial values; and the last five methods depend on neither the infinity nor the initial values.

Each of the simple relationships which are given by Eqs. 17 through 19 also have their inherent disadvantages. The simple first-order relationship which is given by Eq. 16 places emphasis on the initial reading and, therefore, it is not accurate when A_T is nearly equal to A_{INT} or when A_T is very small. The methods given by Eq. 18 and by Eq. 19 calculate the rate constant from pairs of data points, and, when they are used over all of the data points, then they will give an average rate constant which approaches a value which would be calculated if only the initial and infinity data points were used. However, the initial and infinity data points are the least accurate. When Eq. 17 is used to calculate a rate constant for each data point, then these least accurate data points are

again emphasized. Of course, when Eq. 17 is used in the usual graphical method of plotting $\ln(A_{INF}-A_T)$ versus the time, then much of this dependence is eliminated.

In addition to calculating the rate constants by the different methods, the program calculates the half-life in the units of seconds, minutes and hours and also the standard deviations of each rate constant. After the computer calculates the least squares rate constant by Method (a), then the least squares absorption value, AL, is calculated by Eq. 22. The difference between the calculated, AL, and the experimental absorption, A_T, values is determined. The computer then prints the experimental time and the experimental absorption value, the calculated absorption value and the difference between the two absorption values for each data point given the computer. After the average rate constants are calculated by Methods (d) and (e), then the difference between the average rate constant and the rate constant calculated for each experimental data point is determined. The values for each of these quantities are printed. Comparisons of all of these values show which experimental data points are in poor agreement.

Experimental Procedure Seeking Evidence for Complex Formation

Evidence for complex formation was sought by recording the nuclear magnetic resonance and ultraviolet spectra of the two reactants and also of the mixtures of the two reactants and by performing a limited number of kinetic experiments.

The nuclear magnetic resonance experiments were performed by recording the spectra of the complexing reagent and of the diazonium salt in acetone-d_6 separately, using tetramethylsilane as the reference. A

potential complexing reagent was added to the solution of the diazonium salt, and the spectrum of this solution was recorded with the Varian A-60 instrument.

The ultraviolet spectra studies consisted of carefully making up solutions of the diazonium salts and of the complexing reagent in aqueous, monobasic potassium phosphate buffered solutions. After recording the spectra of the two reactants, equal volumes of the two solutions were mixed, and the spectrum of the mixture was recorded with the Cary 14 spectrophotometer. This spectrum was compared with the one obtained by mechanically adding the spectra of the two reactants in the separate solutions.

Experiments which were designed to determine the effect of the different buffers (phosphoric acid, acetic acid, monobasic potassium phosphate) and of potassium iodide in monobasic potassium phosphate buffered solution were performed by making up solutions of the diazonium salts, by recording their spectra and by calculating the molar extinction coefficients of the diazonium salts.

The kinetic experiments were performed according to Procedure IV, except that the potential complexing reagent was added to the solution.

Miscellaneous Reactions

The miscellaneous reactions of the diazonium salts consisted of the reactions with 3-azabicyclo(3.2.2.)nonane, with potassium iodide and with hydrogen peroxide.

The reaction of the diazonium salt with the bicyclic compound was performed by dissolving 5.00×10^{-3} mole of the 3-azabicyclo(3.2.2.)nonane in 50 ml. of dry methanol and by adding to this solution 5.00×10^{-3}

mole of the diazonium salt. This solution was allowed to stand at room temperature for thirty minutes. The precipitate was collected by filtration and washed with an additional 10 ml. of methanol. After the product was dried under vacuum, the nuclear magnetic resonance spectra of the triazenes were recorded.

The reaction with potassium iodide was performed by dissolving 1.00×10^{-2} mole of this reagent and 1.00×10^{-2} mole of monobasic potassium phosphate in 100 ml. of water and by adding to this solution 5.00×10^{-3} mole of the diazonium salt. After this solution stood at room temperature for thirty minutes, the substituted iodobenzene was collected by filtration.

The reaction with aqueous 30 per cent hydrogen peroxide solution was carried out by dissolving 5.00×10^{-3} mole of the diazonium salt and 1.00×10^{-2} mole of monobasic potassium phosphate in 50 ml. of water and by adding to this solution 5 ml. of 30 per cent hydrogen peroxide solution. The resulting solution was allowed to stand at room temperature for one hour. The solid formed by this reaction was collected by filtration and was washed with acetone. From this washing, a white solid was collected which did not melt up to 250° C and was not soluble in the common organic solvents. The evaporation of the acetone afforded a dark brown viscous liquid.

CHAPTER VI

EXPERIMENTAL RESULTS

Physical Constants for the Diazonium Salts and Complexing Reagents

Table 2 summarizes the position of the absorption maxima and their molar extinction coefficients in monobasic potassium phosphate buffered aqueous solutions, for the experimental and the literature melting points[87,88] for the five diazonium salts which were used in our kinetic studies, and for the two additional diazonium salts which were used in our studies seeking evidence for complex formation.

Table 3 summarizes the experimental yields and melting points for the investigation of our alkylation and decarboxylation procedures. The decarboxylation procedure did not yield satisfactory results for some of the amines and, therefore, data are not presented for these attempted decarboxylations.

The positions of the absorption maxima and their extinction coefficients are summarized in Table 4 for the two tertiary amines which were prepared by our alkylation-decarboxylation procedure, for 4-nitrodimethylaniline, and for the Baker Analyzed Grade potassium iodide.

Studies with TMPD

In Chapter IV, the original, general purpose of this work was stated

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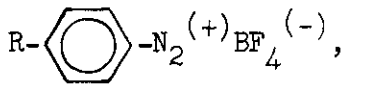
[87]D. Y. Curtin and J. L. Tueton, J. Org. Chem., 26, 1794 (1961).

[88]A. Roe, "Organic Reaction," John Wiley and Sons, New York, vol. 5, p. 198.

Table 2

The Physical Constants for the Diazonium Salts

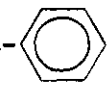
Diazonium Salt,



Where R- is,	Absorption Maximum: Position Millimicrons, mμ.	Absorption Maximum: Extinction Coefficient, e.	Melting Points in °C: Experimental	Ref. 87	Ref. 88
H-	262	12,400	109.5-110.5	100	100
O_2N-	260	16,600	156.5-157.0	154	156
CH_3O-	315	23,600	146.4-147.7	142	139
Cl-	282	17,000	139.0-139.5	139	---
CH_3-	279	15,600	112.5-113.5	---	110
Br-	292	17,600	132.0-133.0	---	133
I-	326	12,500	----------	---	---

Table 3

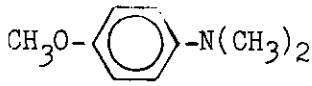
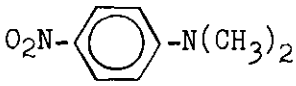
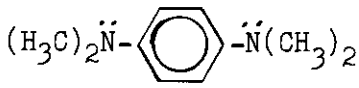
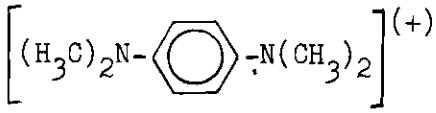
Data for Alkylation and Decarboxylation Reactions

The Amine, R-  -NH_2, and the 2-Chloroaliphatic acid R'HC(Cl)CO_2H.

Where		Alkylation		Decarboxylation	
R-is,	and R'- is,	yield, per cent	melting point, °C	yield per cent	melting point, °C
CH_3O-	H-	80	77-82	45	43.8-44.8
NH_2-	H-	55	165-167	52	51.0-52.0
H-	H-	25	66-68		
Cl-	H-	50	85-90		
CH_3-	H-	55	128-130		
NH_2-	CH_3-	30	185-192		
CH_3O-	CH_3-	35	185-190		

Table 4

The Physical Constants for the Complexing Reagents

Complexing Reagent	Absorption Position, millimicrons, mμ.	Extinction Coefficient, e.
KI	226	17,700
	275	860
	225	485
	425	830
	260	
(TMPD)	322	
	260	
	322	
(Radical-cation, Wurster's Blue Cation)	560	12,500
	610	12,000

to be the study of the reaction between TMPD and the diazonium salts. More specifically, the first experiments were designed to determine if conditions could be found under which a stoichiometric reaction occurs between the diazonium salts and TMPD. A digest of the results concerning the stoichiometry of the reaction is given in Table 5 in terms of the ratio of the maximum concentration of the radical cation produced to the initial concentration of the diazonium salt, (Rad.)/(Diaz.). The last column gives the range of values for which this stoichiometry was investigated in terms of the ratio of the initial concentrations of the two reactants. If a range of values is not given, the values represent only one experiment.

Since the experimental results which are given in Table 5 failed to define reaction conditions under which diazonium ions are reduced by TMPD with clean stoichiometry, kinetic studies of the rate of radical production were undertaken in an attempt to isolate separate events in the complex chain of reactions.

All of the studies between these two reactants in buffered, aqueous solution showed an immediate, rapid, initial reaction which was usually complete within ten seconds after mixing. After this rapid, initial reaction, a second, slower reaction took place to give, usually, a maximum concentration of the radical. As our efforts to deoxygenate and to exclude other trace impurities from the solution improved, both the initial and the maximum concentration of the radical, $TMPD^{(+)}$, decreased, but the same general behavior was always observed. Table 6 summarizes the results of some of the individual experiments. This table gives the ratio of (Rad.)/(Diaz.) at the initial mixing of the reactants and after the

Table 5

Stoichiometric Studies between TMPD and Diazonium Salts

Procedure	Buffer	(Rad.)/(Diaz.)	(Amine)/(Diaz.) minimum	maximum
4-Nitrobenzenediazonium Tetrafluoroborate				
I	KHP	1.0	3.0	20.0
I	none	2.0	3.0	8.0
II	KHP	0.42	1.5	6.0
IV	KH_2PO_4	0.55	3.4	3.8
4-Methoxybenzenediazonium Tetrafluoroborate				
I	KHP	2.0	6.0	15.0
I	none	3.0	10.0	25.0
III	KH_2PO_4	0.54	1.7	
IV	KH_2PO_4	1.65	10.0	
Benzenediazonium Tetrafluoroborate				
I	KHP	0.84	4.0	30.0
I	none	1.0	4.0	15.0
III	KH_2PO_4	0.51	53.0	
IV	KH_2PO_4	0.60	3.0	51.0
4-Chlorobenzenediazonium Tetrafluoroborate				
I	KHP	1.7	6.0	15.0
I	none	1.9	10.0	30.0

Table 6

Time Studies for the Appearance of the Radical-cation

Procedure	Buffer	(Rad.)/(Diaz.) Initial	Later	Time in Hours.
4-Nitrobenzenediazonium Tetrafluoroborate				
II	none	0.50	1.00	3
II	none	0.25	0.50	3
II	none	0.21	0.70	11
IV	KH_2PO_4	0.26	0.62	30 *
IV	KH_2PO_4	0.29	0.48	25 *
4-Methoxybenzenediazonium Tetrafluoroborate				
III	KH_2PO_4	0.48	0.54	7 *
IV	KH_2PO_4	1.34	1.65	2 *
Benzenediazonium Tetrafluoroborate				
II	none	0.27	0.77	12
II	none	0.16	1.00	9
III	KH_2PO_4	0.41	0.51	10 *
IV	KH_2PO_4	0.018	0.41	5 *
IV	KH_2PO_4	0.57	0.62	4 *
IV	KH_2PO_4	0.014	0.57	164
4-Chlorobenzenediazonium Tetrafluoroborate				
II	none	0.66	0.94	7
II	none	0.42	0.56	10

*Maximum concentration of the radical was observed.

reactants had been allowed to react for the time stated in the last column. If the ratio at the time stated represents a maximum for the particular study, an asterisk appears beside this time.

One series of experiments was performed by adding the 4-methoxybenzenediazonium salt to a solution of the oxidized amine, $TMPD^{(+)}ClO_4^{(-)}$, according to Procedure I. The results showed that the concentration of the radical decreased with increasing concentration of the diazonium salt.

Kinetic and Product Studies

Simultaneously with the TMPD studies, other experiments were performed in the absence of the amine so that the rate of appearance of the radical cation could be compared with the rate of decomposition of the diazonium salts under the same experimental conditions. It quickly became apparent from these studies that both the products observed and the rate of decomposition of the diazonium salts are very dependent upon the exact experimental conditions. Accordingly, more than 80 experiments were performed in the absence of the amine in the hope of refining the reaction medium and of determining the influence of the various other factors.

The data from these experiments were analyzed statistically with a computer to determine if meaningful rate constants could be calculated. The products were identified by their ultraviolet absorption spectra, measured on the samples used for kinetic runs after the reaction was completed. In some cases these results were verified by preparative scale product isolations.

Except for the unsubstituted and the 4-methylbenzenediazonium tetrafluoroborate, the rate constants calculated on the Burroughs 5500 computer

were not reproducible. In preference to citing the more than 880 calculated rate constants, only examples will be given in Tables 7-10. Emphasis is placed on the important conclusions which can be drawn from the observed products and from the influence of the reaction medium on the course of the reaction.

The rate constants given in Tables 7-10 for the decomposition of the diazonium salts in aqueous, buffered solution were derived from experiments performed according to Procedure IV. The letters refer to the mathematical method used to calculate the rate constant. These methods have been described in Chapter V.

Each diazonium salt responded differently to a particular reaction medium, and, therefore, this influence is discussed separately for each diazonium salt.

Both the products and the rate constants which were obtained with the decomposition of the 4-nitrobenzenediazonium tetrafluoroborate depend on the buffer, on the trace impurities, and on other compounds which are present in solution.

The dependence on the buffer is shown by the observed products when this diazonium salt is allowed to decompose in two different, buffered, deoxygenated, aqueous solutions. The products are 4-nitrophenylacetate and 4-nitrophenol when equimolar concentrations of sodium acetate-acetic acid and monobasic potassium phosphate are used as the buffer reagents, respectively.

The rate plots for the decomposition of 4-nitrobenzenediazonium tetrafluoroborate showed large deviations when Procedure III was used. Since this behavior could be explained by the decomposition of the

Table 7

Kinetic Rate Constants for the Decomposition of Benzenediazonium Tetrafluoroborate at 30.0±0.01° C

Rates are x 10^{-4} $sec.^{-1}$

Mathematical Method	Buffer					
	HOAc-NaOAc, 0.1 M	HOAc-NaOAc, 0.01 M	KH_2PO_4, 0.1 M	KH_2PO_4, 0.1 M	KH_2PO_4, 0.1 M	KH_2PO_4 0.01 M
a	1.24	1.15	0.97	0.96	0.84	0.61
b	1.24	1.02	1.02	0.96	0.92	0.58
c	1.23	1.26	0.95	1.13	0.83	0.73
d	1.37	1.28	1.14	0.96	0.94	0.86
e	1.00	0.97	0.87	0.79	0.64	0.67
f	0.67	0.70	0.67	0.65	0.50	0.31
g	0.69	0.70	0.64	0.65	0.51	0.31
h	0.68	0.71	0.64	0.72	0.55	0.52
i	0.69	0.69	0.62	0.77	0.73	0.59
j	0.69	0.70	0.64	0.79	0.52	0.56
k	0.67	0.61	0.65	0.63	0.54	0.26

Table 8

Kinetic Rate Constants for the Decomposition of 4-Methylbenzenediazonium Tetrafluoroborate at 30.0±0.01° C

Rates are x 10^{-5} $sec.^{-1}$

Mathematical Method	Buffer				
	HOAc-NaOAc, 0.1 M	HOAc-NaOAc, 0.01 M	KH_2PO_4, 0.1 M	KH_2PO_4, 0.1 M	KH_2PO_4 0.01 M
a	1.04	1.10	1.26	1.00	1.32
b	1.05	1.17	1.56	0.90	1.30
c	1.06	1.18	0.23	0.99	1.22
d	1.21	1.26	2.11	0.85	1.90
e	0.99	1.06	1.64	0.76	1.64
f	0.64	0.78	0.89	0.80	0.90
g	0.64	0.78	1.11	0.80	0.90
h	0.74	0.84	1.45	0.80	0.93
i	0.78	0.95	1.97	0.91	1.00
j	0.76	0.82	1.65	0.79	0.95
k	0.51	0.71	1.22	0.69	0.20

Table 9

Kinetic Rate Constants for the Decomposition of the 4-Nitrobenzenediazonium Tetrafluoroborate at 30.0±0.01° C

Rates are x 10^{-5} $sec.^{-1}$

Mathematical Methods	Buffer					
	HOAc-NaOAc, 0.1 M	HOAc-NaOAc, 0.01 M	HOAc-NaOAc, 0.01M	KH_2PO_4, 0.1 M	KH_2PO_4, 0.01 M	KH_2PO_4 0.01 M
a	2.08	3.34	0.47	0.55	0.45	0.15
b	1.41	2.81	0.46	0.11	0.69	0.16
c	1.55	4.14	0.32	7.26	0.37	0.27
d	0.51	2.22	0.40	4.52	0.38	0.57
e	0.35	1.69	0.30	2.42	0.24	0.35
f	1.29	1.99	0.23	0.14	0.19	0.07
g	1.29	2.02	0.23	0.14	0.19	0.07
h	1.07	2.96	0.22	2.39	0.19	0.12
i	1.00	3.39	0.26	4.53	0.23	0.17
j	1.06	3.22	0.22	4.27	0.20	0.14
k	0.84	1.42	0.19	0.058	0.095	0.082

Table 10

Kinetic Rate Constants for the Decomposition of the 4-Methoxybenzenediazonium Tetrafluoroborate at 30.0±0.01° C

Rates are x 10^{-6} sec. $^{-1}$

Mathematical Methods	Buffer			
	HOAc-NaOAc, 0.1 M	HOAc-NaOAc, 0.01 M	KH_2PO_4, 0.1 M	KH_2PO_4 0.01 M
a	0.84	0.75	0.78	0.81
b	0.20	1.14	0.33	1.13
c	0.87	0.46	1.02	0.89
d	2.37	0.05	1.53	2.14
e	2.26	0.05	1.27	1.41
f	0.80	0.54	0.63	0.49
g	0.80	0.54	0.63	0.49
h	0.95	0.58	0.74	0.65
i	2.04	0.70	1.16	1.19
j	0.86	0.58	0.72	0.70
k	0.18	0.55	0.26	0.40

diazonium salt in that the salt was sensitive to the oxygen present, we determined the rate constants for a solution which had been degassed according to Procedure IV and for the same solution through which compressed air had been passed. The ratios of the rate constants in the presence and absence of air were 5.0 and 70.0 for the acetate and phosphate buffers, respectively. To further test this sensitivity to oxygen and oxidizing agents, 5 ml. of 30 per cent hydrogen peroxide solution were added to 50 ml. of a phosphate-buffered solution. Immediately following the addition of the hydrogen peroxide solution, a rapid reaction occurred which was complete within two minutes. Examination of the ultraviolet spectrum of this solution revealed 4-nitrophenol to be one of the products.

A preparative scale experiment yielded 4-nitrophenol, a white material and a viscous, brown material as the products. The latter two substances were obtained from the solid precipitated from the reaction mixture. The white material was not soluble in acetone, which was used to wash the original solid, and evaporation of the acetone left the viscous, brown material. The white material did not melt up to 250° C, and it was not soluble in any common organic solvent. The deeply colored, viscous material appeared to be a complex mixture of compounds from its nuclear magnetic resonance spectrum. Therefore, we have not positively identified either of these products.

The decomposition of this diazonium salt in the presence of potassium iodide, 4-methoxy- and 4-nitrodimethylaniline in monobasic potassium phosphate buffered solutions gave rate constants which were all smaller in magnitude than the rate constant for the decomposition of the diazonium

salt in the absence of these compounds. The ratios of the rate constants in the absence and presence of these compounds were 5.4, 1.5 and 2.5, respectively. A preparative scale experiment utilizing potassium iodide and the diazonium salt as reactants revealed a quantitative conversion to 4-nitroiodobenzene which agreed with the final ultraviolet spectrum of the kinetic studies. Preparative scale experiments were impossible with the other two compounds due to their low solubility in water. The reaction products could not be identified from the spectrum of the kinetic study solutions.

The 4-methoxybenzenediazonium tetrafluoroborate did not show the same behavior towards changes in the reaction medium as the 4-nitrobenzenediazonium salt. The reaction product was the expected 4-methoxyphenol, regardless of the buffer used. Its sensitivity towards oxygen was complicated by some factor which has not been clearly identified at this time, but it is possibly caused by trace amounts of a metal cation such as the cuprous cation. Using Procedure III, the rate plots showed deviations, just as the 4-nitrobenzenediazonium salt did. However, as our ability to deoxygenate the solution and to prepare the reactants, solvents and reaction vessels in a pure state improved, the rate of decomposition and sensitivity to molecular oxygen showed a remarkable decrease.

For example, two buffered solutions of this diazonium salt were prepared according to Procedure IV. The first was deoxygenated in the normal manner, and the second solution was saturated with oxygen gas. The solution saturated with oxygen showed very little evidence of decomposition after 96 hours, while the deoxygenated solution indicated a very slow rate of decomposition. No attempt was made to calculate rate constants for

these extremely slow reactions.

Although it was not as extensively investigated as the 4-methoxybenzenediazonium salt, the 4-chlorobenzenediazonium salt showed the same general behavior. The expected phenol was the observed product regardless of the buffer, and the rate constants for the decomposition decreased as the experimental techniques improved.

The unsubstituted and 4-methylbenzenediazonium salts are less sensitive to the buffer, molecular oxygen and other compounds. Both decomposed with reproducible rate constants to the expected, corresponding phenol in the presence and absence of oxygen.

The two remaining diazonium salts, the 4-bromo- and 4-iodobenzenediazonium tetrafluoroborates, were not investigated by the kinetic and product experimental methods. However, these diazonium salts, together with the other diazonium salts, were used in the experiments which sought evidence of complex formation.

Ultraviolet Spectra Studies

After the influence of the reaction medium had been demonstrated by the kinetic and product studies, we undertook the investigation of other systems in hope of finding evidence for an association between the diazonium salts and other compounds.

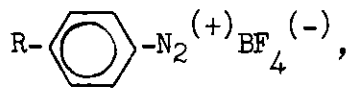
The first ultraviolet studies consisted of carefully making up solutions of the diazonium salts and determining their molar extinction coefficients in five different solutions. The results of these studies are given in Table 11. The buffer reagents were monobasic potassium phosphate, phosphoric acid, acetic acid and equimolar sodium acetate-acetic acid. A solution of potassium iodide which used monobasic

Table 11

Extinction Coefficients of the Diazonium Salts

Buffer Concentrations are 0.10 M.

Diazonium Salt,



where R- is	KH_2PO_4	H_3PO_4	HOAc	HOAc-NaOAc	KI
I-	12,500	12,700	12,170	12,750	8,880
Br-	17,600	17,000	17,200	18,250	15,600
Cl-	17,000	18,000	17,600	17,500	18,250
H-	12,400	12,500	12,200	13,400	12,400
O_2N-	16,600	16,250	16,500	15,400	17,200
CH_3O-	23,600	------	29,500	30,300	26,650
CH_3-	15,600	------	15,500	------	------

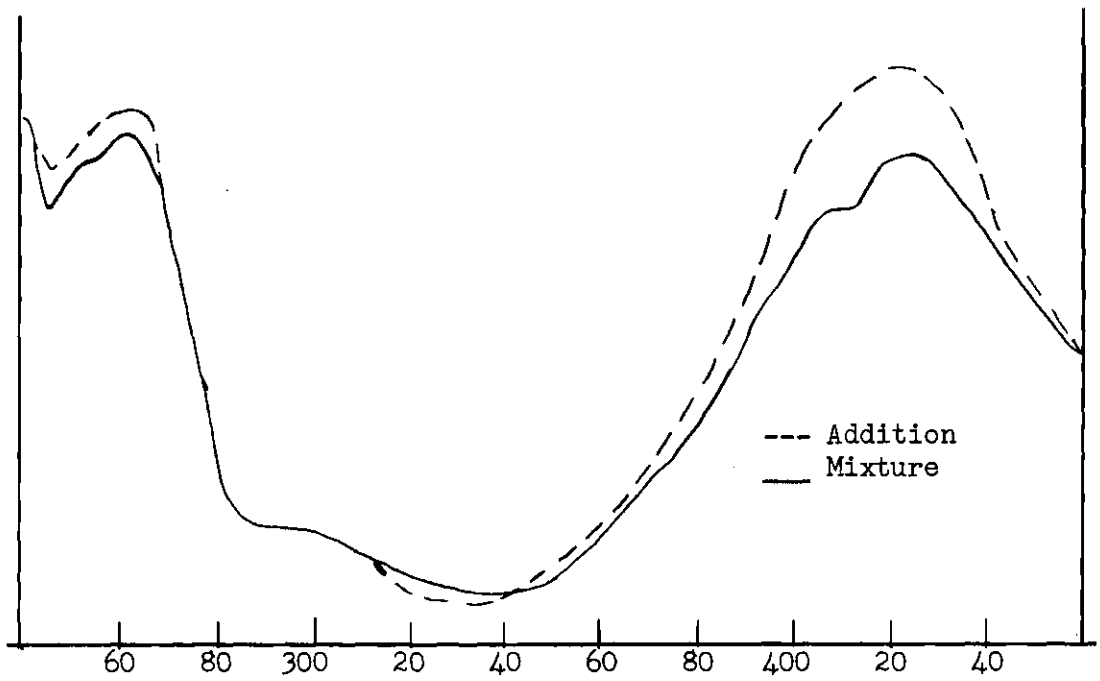


Figure 3. UV of Benzenediazonium Tetrafluoroborate and 4-Nitrodimethylaniline

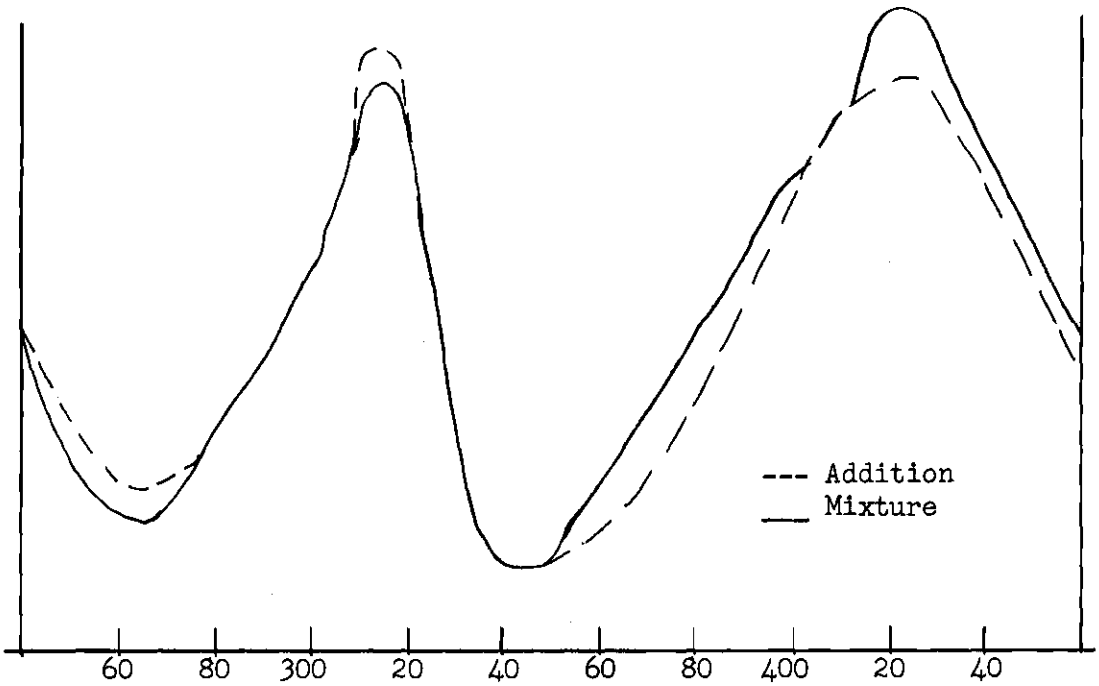


Figure 4. UV of 4-Methoxybenzenediazonium Tetrafluoroborate and 4-Nitrodimethylaniline

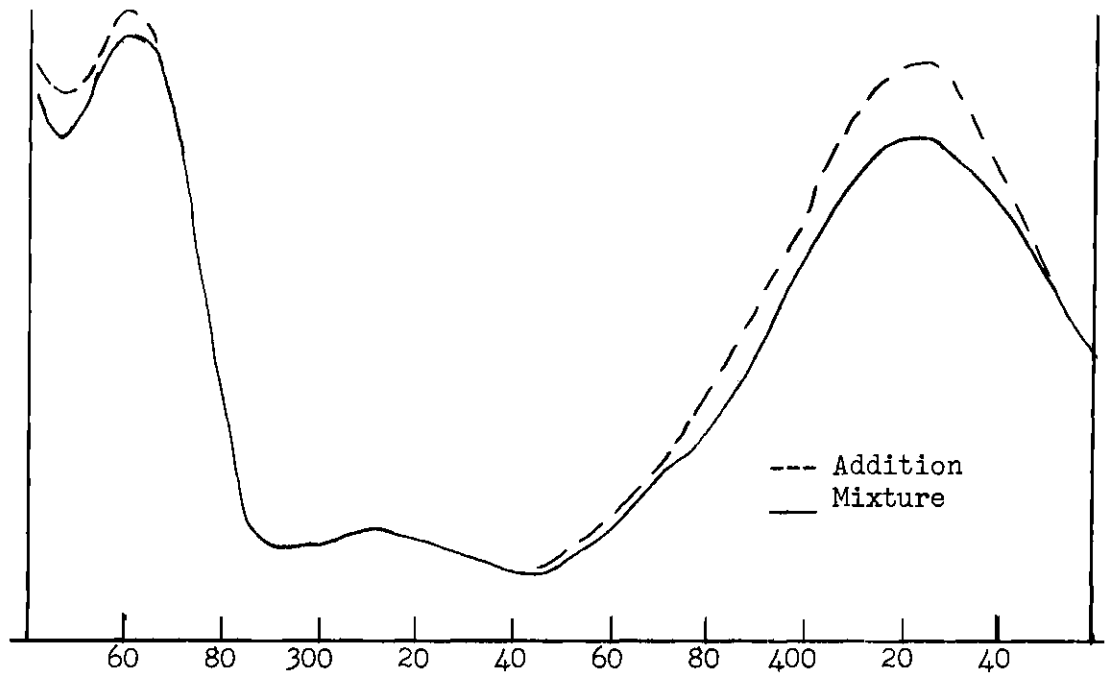


Figure 5. UV of 4-Nitrobenzenediazonium Tetrafluoroborate and 4-Nitrodimethylaniline

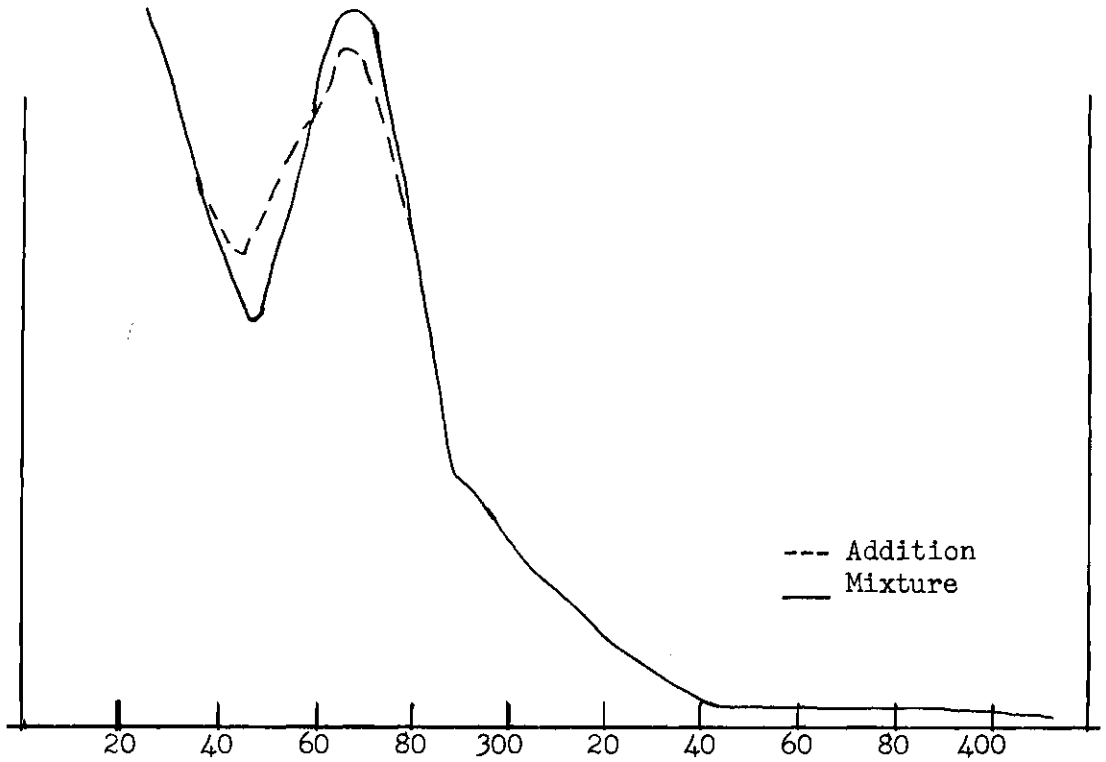


Figure 6. UV of Benzenediazonium Tetrafluoroborate and 4-Methoxydimethylaniline

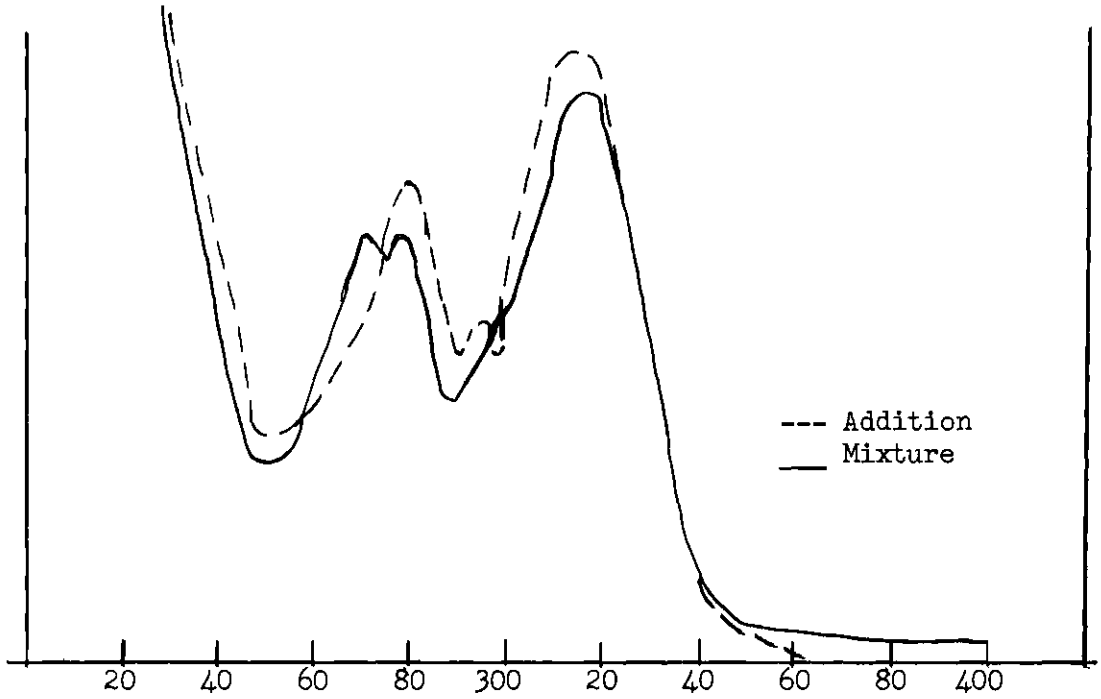


Figure 7. UV of 4-Methoxybenzenediazonium Tetrafluoroborate and 4-Methoxydimethylaniline

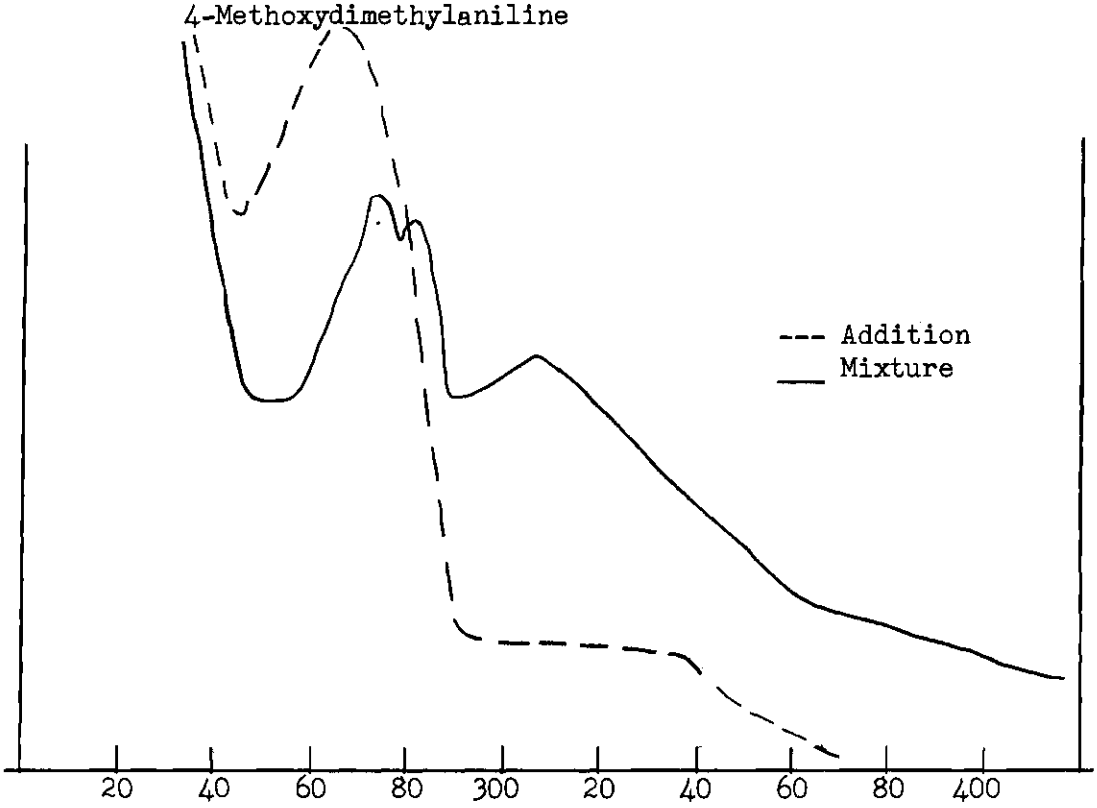


Figure 8. UV of 4-Nitrobenzenediazonium Tetrafluoroborate and 4-Methoxydimethylaniline

potassium phosphate as the buffer was the fifth solution.

The second ultraviolet studies consisted of preparing aqueous, monobasic potassium phosphate buffered solutions of 4-nitro- and 4-methoxydimethylaniline and of three diazonium salts. These were the unsubstituted, the 4-nitro- and 4-methoxybenzenediazonium tetrafluoroborates. Examination of the spectra for the separate compounds and for the mixtures showed that the absorption peaks overlapped too badly to permit the accurate determination of their molar extinction coefficients. However, these spectra did indicate that an association in some cases and possibly a chemical reaction in one case had taken place.

When a solution of 4-nitrodimethylaniline was added to the solutions of the three diazonium salts, a possible association between the reactants was shown by a change in the molar extinction coefficient of the absorption peak of the donor which is located at 425 mu. The unsubstituted and 4-nitrobenzenediazonium salts showed a decrease, while the 4-methoxybenzenediazonium salt showed an increase. Figures 3, 4 and 5 give the spectra for the solutions where both reactants are present and also show the spectra which are obtained by mechanically adding the spectra of the individual solutions.

When the 4-methoxydimethylaniline solution was added to a solution of the 4-nitrobenzenediazonium salt, an immediate change was indicated by the appearance of a new peak at 310 mu. This new peak is located at the same wavelength as that of the absorption peak of 4-nitrophenol. However, we do not have any experimental evidence at this time to distinguish between the two possibilities, that is, either a complex or a product formation. The other two diazonium salts showed no pronounced

change when they were added to this potential complexing agent. Figures 6, 7 and 8 give the spectra for these studies.

Nuclear Magnetic Resonance Studies

The proton magnetic resonance spectra of the diazonium salts and of some potential electron donors were determined and evidence of reaction between these sought by comparing the spectra of mixtures of these components with the spectra of the separate components. Several types of behavior were observed.

In some cases the spectra were additive, suggesting that no interaction had occurred. In other cases, changes in the chemical shifts for the protons in the components gave evidence of complex formation. In still others, gross spectral changes, such as line-broadening and the appearance of new absorptions, signalled extensive chemical reactions. In the latter cases, changes in the solutions were generally observed visually as well.

Extensive chemical reaction was observed when either 4-methoxydimethylaniline or TMPD was added to the acetone-d_6 solution of any of the seven diazonium salts. The resulting solutions immediately became a deep purple and a gas was evolved. A similar but less vigorous behavior was observed when 4-methoxynitrobenzene was added to an acetone-d_6 solution of 4-chlorobenzenediazonium tetrafluoroborate. All of the resulting spectra indicated that a complex reaction had taken place, the products of which could not be readily identified from their spectra.

The chemical shifts for the diazonium salts and the complexing reagents are summarized in Table 12 for mixtures of the two reactants.

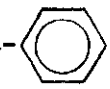
The results given in Table 12 should be compared with the results

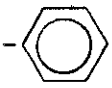
obtained for the individual components. The chemical shifts for the diazonium salts and the complexing reagents in separate solutions are given in Tables 13 and 14, respectively.

Tables 15 through 17 summarize the proton magnetic spectra for the nitro compounds which correspond to the diazonium salts, for the triazenes prepared from four of the diazonium salts and 9-azobicyclo-(3.2.2.)nonane, and for the 4-substituted anilines used to prepare the diazonium salts.

Table 12

Nuclear Magnetic Resonance Studies for Possible Complex Formation

Diazonium Salts, R-  $-N_2^{(+)}BF_4^{(-)}$, and Complexing Reagents,

R'-  $-NO_2$, where R- is, R'-is.

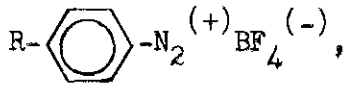
Absorption, δ ppm., and the Coupling Constants, J, arising from the

		Diazonium Salt,				Complexing Reagent.			
		δ	δ	δ	J	δ	δ	δ	J
O_2N-	$(CH_3)_2N$-		8.79	9.14	9.0	3.14	6.68	8.07	9.5
CH_3O-	Br-	4.12	7.50	8.76	9.5		7.84	8.18	9.5
CH_3O-	Cl-	4.16	7.43	8.70	---		7.68	8.27	9.5
CH_3O-	CH_3-	4.12	(7.56)	8.74	9.5	2.44	7.41	8.08	9.0
CH_3O-	$(CH_3)_2N$-	4.16	7.52	8.76	9.5	3.14	6.78	8.08	9.5
CH_3O-	CH_3O-	4.16	7.54	8.68	9.5	3.97	7.15	8.23	9.0
Br-	CH_3O-		(8.28)	8.74	9.0	3.93	7.08	8.17	9.0
I-	CH_3O-		8.38	----		3.94	7.02	8.19	9.0
CH_3-	CH_3O-	2.62	7.85	8.66	9.0	3.92	7.11	8.19	9.5
CH_3-	$(CH_3)_2N$-	2.58	7.82	8.64	9.0	3.09	6.74	8.06	9.5

Table 13

Nuclear Magnetic Resonance Studies of the Diazonium Salts

Diazonium Salts,



where R- is,

	Absorption Positions, δ ppm., and Coupling Constants, J.			
	δ	δ	δ	J
CH_3O-	4.18	7.56	8.84	9.5
CH_3-	2.67	7.85	8.68	8.5
Cl-		8.12	8.86	8.0
Br-		8.28	8.77	9.5
I-		8.54	----	
O_2N-		8.86	9.22	9.5
H-		~8.4		

Table 14

Nuclear Magnetic Resonance Studies of the Complexing Reagents

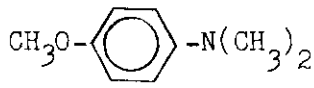
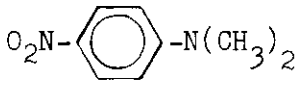
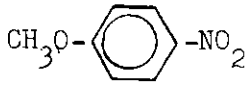
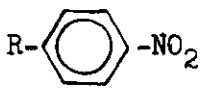
Complexing Reagent	Absorption Positions, δ ppm., and Coupling Constants, J.			
	δ	δ	δ	J
	2.81	3.68	6.71	
	3.12	6.74	8.02	9.5
	2.73	6.65	----	
	4.02	7.06	8.06	9.5

Table 15

Nuclear Magnetic Resonance Studies for the Compounds where the Diazonium Function has been replaced with the Nitro Function

The Nitrobenzenes,



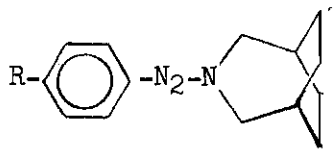
Absorption Positions, δ ppm., and Coupling Constants, J cps.

where R- is,	δ	δ	δ	J
O_2N-		8.38	----	
Br-		7.84	8.18	9.5
Cl-		7.65	8.24	9.0
CH_3-	2.43	7.41	8.08	9.0
I-		7.92	----	
CH_3O-	4.02	7.06	8.06	9.5

Table 16

Nuclear Magnetic Resonance Studies for the Triazenes

The Triazenes,



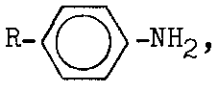
where R- is, Melting Points in °C, Absorption Positions, δ ppm., and Coupling Constants, J cps.

R-	Melting Points in °C	δ	δ	δ	δ	δ	J
O_2N-	141.0-142.0	1.70	2.11	4.06	7.45	8.17	9.0
Cl-	90.5- 91.0	1.66	2.10	3.94	7.30	7.36	
Br-	90.5- 91.5	1.64	2.16	4.02	7.37	7.40	
I-	105.0-105.5	1.72	2.14	4.01	7.17	7.64	9.0

Table 17

Nuclear Magnetic Resonance Studies of the Anilines

The Anilines,



Absorption Positions, δ ppm., and Coupling Constants, J cps.

where R- is,	δ	δ	δ	δ	J
CH_3O-	3.39	3.69	6.62	6.67	
Cl-		3.56	6.52	7.07	9.0
O_2N-		----	6.65	8.08	9.0
Br-		3.56	6.45	7.17	9.0
CH_3-	2.29	3.41	6.54	6.94	8.5

CHAPTER VII

DISCUSSION OF EXPERIMENTAL RESULTS

Preparation of Diazonium Salts and Complexing Reagents

The different methods which may be used to prepare the diazonium salts have been recently reviewed.[1,88] These methods differ in their use of starting reagents, of solvents, of diazotization reagents and of means for the introduction of the anion. The majority of these reactions start with the primary aromatic amine which corresponds to the desired diazonium salt. This amine is reacted with nitrous acid or a nitrosating agent, such as nitrosyl fluoroborate or n-butyl nitrite.

In some more recently developed methods, a nitroso group is introduced directly into the aromatic nucleus by means of an electrophilic substitution with a nitrosating reagent such as nitrosyl chloride or nitrosyl perchlorate.[89-92] Further treatment with two moles of nitrous acid converts the nitroso function into the diazonium nitrate.

After carefully considering the merits of the above methods for preparing the diazonium salts, we decided to use the well-known method of reacting the aromatic amine with n-butylnitrite in the presence of fluoroboric acid. The fluoroborate salt was desired since diazonium

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[89]H. P. Patel and J. M. Tedder, J. Chem. Soc., 1963, 4889.

[90]J. M. Tedder and G. Theaker, Tetrahedron, 5, 288 (1957).

[91]R. M. Schibner, J. Org. Chem., 29, 3429 (1964).

[92]K. Bott, Angewandte Chemie, 77, 132 (1965).

fluoroborates frequently form stable crystal lattices which make them suitable for isolation and purification, and it is unlikely that the fluoroborate anion would complicate the reactions studied. Since it was desired to prepare the diazonium salts in a pure state free from both inorganic and organic impurities, attention was given to purification of the reactants and solvents and to the suitability of various solvents as the reaction medium.

In particular, attention was paid to eliminate compounds which are known to catalyze or influence the decomposition of the diazonium salts. For example, trace amounts of cuprous chloride greatly catalyze the decomposition of the 4-nitrobenzenediazonium salt in both aqueous and acetone solutions. The acetate anion and alcohols also frequently encourage a free radical pathway. Other workers have established that benzenediazonium chloride is stable for extended periods of time when it is stored under anhydrous ether in an icebox or when it is placed in a stopped bottle, at room temperature, under dry dioxane.[93] However, the effect of aliphatic peroxides, such as those found in diethyl ether which has been exposed to sunlight and the atmosphere, has not been clearly defined.

Since the diazonium salts are known to react with acetone and diethyl ether under some conditions, we briefly considered the use of other solvents such as chloroform and nitromethane. However, the solubility characteristics of the reactants did not lend themselves to the use of these new solvents. We, therefore, used acetone and diethyl

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[93]W. Smith and C. E. Warning, J. Am. Chem. Soc., 64, 469 (1942).

ether which had been purified by distillation from phosphorus pentoxide and lithium aluminum hydride, respectively.

The results of our efforts to prepare the diazonium salts in a pure state are indicated by the melting points reported in Table 2. Except for the 4-bromobenzenediazonium salt, our experimental melting points are all higher than the values reported in the literature. All of our diazonium salts were crystalline and white, except for the 4-nitrobenzenediazonium salt, which was light yellow.

The difference between our experimental results and those reported in the literature could be due in part to our efforts to prepare the diazonium salts in a pure state. However, direct comparisons between our results and those reported in the literature are impossible because the experimental details for the preparation of the diazonium salts are not given in the literature for specific experiments.

A review of the literature reveals that there are many reported examples of reactions in the literature where other reactions similar to the one given by Eq. 13, the alkylation of amines, have been carried out. For example, various 2-haloacetic acids,[94-97] several substituted beta-propiolactones[98] and chloroacetamides[99] have been reacted with a variety

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[94] L. Michaelis and M. P. Schubert, J. Bio. Chem., 115, 221 (1936).

[95] A. T. DeMonilpied, J. Chem. Soc., 87, 435 (1905).

[96] L. Michaelis and M. P. Schubert, J. Bio. Chem., 106, 331 (1934).

[97] T. B. Johnson and R. Bengis, J. Am. Chem. Soc., 33, 745 (1911).

[98] T. L. Gresham and F. W. Shaver, U.S. Patent 2,568,621 (1951).

[99] W. F. Bruce and J. Seifter, U.S. Patent 2,568,141 (1951).

of aromatic amines to give the imino acids. The esters of some of these acids have been condensed with other reagents in the presence of sodium alkoxides to give a variety of heterocyclic compounds.[95,97]

The decarboxylation of imino acids by heating the dry solid acid under vacuum according to Eq. 14 had not been previously reported in the literature. However, the decarboxylation of phenyliminodiacetic acid to N,N-dimethylaniline has been reported by heating the diacid in an acidic, aqueous solution (usually a sulfuric acid solution) in the presence of a transition metal cation such as the ferric cation.[100] While this procedure was claimed to be general and applicable to a large number of compounds, the instructions given by these workers failed to yield satisfactory results in our hands. We have, therefore, relied on the procedure of heating the dry salt to decarboxylate the imino acids.

Table 3 summarizes the experimental results for the alkylation-decarboxylation procedure which was used by us for the preparation of two potential complexing reagents. While we have successfully alkylated a variety of aromatic mono- and diamines, the results of the attempted decarboxylations were disappointing. However, we used this procedure primarily for the preparation of TMPD and the investigation of different reaction conditions could lead to a satisfactory experimental procedure for the decarboxylation in the other cases as well.

Studies with TMPD

Chapter II of this thesis presents a general review of the literature

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[100]Kalle and Co., German Patent 375463, abstracted in P. Friedländer, Fortsch. Teerfarbenfabrid., 14, 400 (1926).

pertinent to the discussion of the reaction between TMPD and the diazonium salts. Experimental results are cited that TMPD is capable of forming complexes with other compounds which can decompose to radical species under certain reaction conditions and that the diazonium salts can associate with other electron donor species under certain reaction conditions so as to initiate a free radical chain reaction.

The first step in these radical chain initiation steps is believed to be one-electron transfer reaction to give either the phenyl radical directly or the intermediate phenylazo radical. If a suitable reductant is present in solution, a radical chain propagation process can take place. In our studies, potential reductants other than TMPD were rigorously excluded in the hope of isolating this initial one-electron transfer reaction. This system could serve as a model for the other radical reactions which occur under ambiguous conditions. To understand the experimental results one would expect to obtain from our experiments with TMPD, it is helpful to refer specifically to the discussion for the reaction between hypophosphorous acid and the diazonium salts. This discussion describes the experimental evidence that one-electron reductions do occur, that this reduction produces radical intermediates, and that these intermediates can react further with the hypophosphorous acid.

These experiments which were performed by Kornblum[21] were chosen for a detailed discussion because, a priori, one would expect many similarities of the reaction pathways to exist between this reaction and our reaction with TMPD, because the experimental factors which influence the hypophosphorous acid reaction have been extensively investigated and because both studies were carried out in acidic, aqueous solutions. How-

ever, the two studies differ in that after the initial electron-transfer reactions the chain propagation sequence with hypophosphorous acid leads to reduction, whereas a similar propagation sequence is ruled out by the stoichiometry which is observed with the TMPD reaction. Let us now examine some of the possibilities that the reactions between TMPD and the diazonium salts can involve.

The first possibility is that the TMPD reduces the diazonium ions to the corresponding hydrazines. This reaction would require four electrons, four moles of TMPD per mole of the diazonium salt, and three protons. Such reductions are known to occur in the presence of the stannous cation[20] and the chromous cation.[30] This possibility is very unlikely for our studies with TMPD since the required stoichiometry was not observed in any experiments and there was no other evidence of hydrazine formation. Therefore, some other reaction or combination of reactions which requires fewer moles of TMPD per mole of diazonium salt must be considered.

The more reasonable reaction pathways would involve the initial one-electron reduction of the diazonium salt to give one of two intermediate radicals. First the phenylazo radical may be formed and reduced further, with eventual coupling to form, for example, tetrazane or tetrazene. Secondly, the phenyl radical may be formed and could then enter into a number of radical or coupling reactions to give reduction products or azo compounds. The properties of some of these possible products can be deduced from the properties of related compounds.

The anticipated behavior of various substituted 1,4-diphenyltetrazanes is indicated by the studies of the other more substituted

tetrazanes.[101,102] Willmarth and Schwartz have determined the equilibrium constants for the dissociation of the substituted 1,1,4,4-tetraphenyl-2,3-dibenzoyltetrazanes into the 1,1-diphenyl-1-benzoylhydrazyl free radical.[101] Their results were consistent with the formation and stabilization of the proposed three-electron bond of the hydrazyl radical. Experimental evidence that the hydrazyl radical exists in solution included the fact that the solution absorbed nitric oxide, that a single new peak was observed in the visible range of 500 to 530 mu, and that electron spin resonance spectra have been observed for these solutions. The stability of these radicals can be correlated in terms of steric and energy factors.[102] Steric hindrance in the 2 and 3 positions and groups such as the nitro function and the benzoyl function increase the stability.

Some other compounds which could possibly be formed from the phenyl azo radical would include substituted azobenzenes, triazenes and phenylazoalkanes. The azobenzene could be formed by the coupling of the phenylazo and the phenyl radicals or by the coupling of the diazonium ion and the phenol which is produced by the solvolysis of the diazonium ion. While azobenzenes are known to be thermodynamically stable under our conditions, the azo linkage can be isomerized and also reacted with other radicals which are present in the solution.[103] The triazenes, diazoamine compounds

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[101]W. K. Wilmarth and N. Schwartz, J. Am. Chem. Soc., 77, 4543, 3551 (1955).

[102]A. L. Buchachenko, "Stable Radicals," Consultants Bureau, New York, 1965, p. 130.

[103]L. B. Jones and G. S. Hammond, J. Am. Chem. Soc., 87, 4220 (1965).

are known to undergo a rearrangement in acidic, aqueous solutions to the aminoazo isomer.[3] However, under other experimental conditions, 1-aryl-3, 3-dimethyltriazenes have been reported to form free radicals which can arylate aromatic compounds.[104] The suggested decomposition pathway involved the formation of a covalent diazo acetate or chloride which can decompose homolytically. The phenylazoalkanes can be interconverted to the corresponding phenylhydrazones under acidic, basic, and radical initiated conditions.[105]

While these possibilities must be considered as competing, side reactions, the small ratio of radicals, $TMPD^{(+)}$, produced to the initial concentration of the diazonium salt discredits the importance of these reactions. Other reactions where TMPD merely serves as a catalyst to initiate the formation of the phenyl radical is more reasonable.

After the phenyl radical is formed, either directly (Eq. 23), or through the phenylazo radical (Eq. 24), several reasonable pathways are possible. The phenyl radical can react with either a second molecule of the diazonium salt (Eq. 25), with the radical cation of TMPD (Eq. 26), with a second mole of TMPD (Eq. 27), with itself (Eq. 30), or with some other radical present in the solution such as molecular oxygen (Eq. 31). The overall result of the reactions between the phenyl radical and a second molecule of the diazonium salt or the radical cation, $TMPD^{(+)}$, is the formation of the phenyl cation, which would then react with the solvent to give the corresponding phenol (Eq. 28). The third possibility

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[104]O. Vogl and C. S. Rondestredt, Jr., J. Am. Chem. Soc., 77, 3067 (1955).

[105]A. J. Bellamy and R. D. Guthrie, J. Chem. Soc., 1965, 3528.

would require the consumption of two moles of TMPD per mole of diazonium salt and would lead to the reduction product, that is, the substituted benzene (Eq. 29). If two phenyl radicals couple, a biaryl would be formed (Eq. 30). Other radicals present in the solution may also react with the phenyl radical to give complex products (Eq. 31).

$$ArN_2^{(+)} + TMPD \longrightarrow Ar\cdot + TMPD^{(+)} \quad \text{(Eq. 23)}$$

$$ArN_2^{(+)} + TMPD \longrightarrow ArN_2\cdot + TMPD^{(+)} \quad \text{(Eq. 24)}$$

$$Ar\cdot + ArN_2^{(+)} \longrightarrow Ar^{(+)} + ArN_2\cdot \quad \text{(Eq. 25)}$$

$$Ar\cdot + TMPD^{(+)} \longrightarrow Ar^{(+)} + TMPD \quad \text{(Eq. 26)}$$

$$Ar\cdot + TMPD \longrightarrow Ar^{(+)} + TMPD^{+} \quad \text{(Eq. 27)}$$

$$Ar^{(+)} + H_2O \longrightarrow Ar\text{-}OH + H^{(+)} \quad \text{(Eq. 28)}$$

$$Ar^{(-)} + H_2O \longrightarrow Ar\text{-}H + OH^{(-)} \quad \text{(Eq. 29)}$$

$$2\ Ar\cdot \longrightarrow Ar\text{-}Ar \quad \text{(Eq. 30)}$$

$$Ar\cdot + O_2 \longrightarrow Ar\text{-}O\text{-}O\cdot \quad \text{(Eq. 31)}$$

The reactions which produce the phenol as the product are the most reasonable because they are consistent with the observed and the expected behavior of the reactions with TMPD. After deoxygenating the buffer solution according to Procedure IV, the TMPD can be added to the buffer solution with no production of the radical cation. However, with addition of the diazonium salt a rapid reaction occurs. These reactions also involve species which are present in the highest concentrations and they

do not require that the ratio of the radical produced to the initial concentration of the diazonium salt be greater than one. A preparative scale experiment with the 4-nitrobenzenediazonium salt allowed the isolation of 4-nitrophenol in a yield greater than 90 per cent, although the ultraviolet spectra of the kinetic study solutions were too complex to allow direct identification of the products by spectral measurements on the reaction mixture. We have not been able to detect any other products from the kinetic study solutions by their ultraviolet spectra.

A slight modification of these general reactions would best account for the experimental results. After the initial electron transfer and the loss of nitrogen, an association between the phenyl radical and the radical cation, $TMPD^{(+)}$, could act to stabilize the phenyl radical. A collision with almost any species in the solution could free TMPD and the phenyl cation, which would react with the solvent to give the observed phenol.

The attractive features of this pathway are that all of the necessary reactants are in close proximity and, therefore, a rapid reaction is possible without involving a chain sequence and that the intermediate reactants are stabilized.

However, this modified pathway cannot account for the entire decomposition of the diazonium salt because the radical of TMPD is formed in all of the experiments and because the ratios of the radical concentration to the diazonium salt concentration are not reproducible and are sensitive to the experimental conditions.

A reasonable explanation for the production of the radical cation

is that the phenyl radical is initially formed by an electron transfer reaction and is then stabilized by an association with the same TMPD radical cation. This association can be disrupted into either the phenyl radical and the TMPD radical cation or the phenyl cation and TMPD. The two intermediates, the phenyl radical and the phenyl cation, could react to give the phenol or by a radical chain pathway to give a variety of products. The exact mode of reaction would be expected to be very dependent on the exact reaction conditions. The important factors include the concentrations and the characteristics of the reactants, the possibility of a photo-induced reaction, the presence of other potential reactants, in particular molecular oxygen, the stability of the proposed complexes, and the rates of these catalyzed decompositions relative to the rate of the simple loss of nitrogen from the diazonium ion to give the phenyl cation directly.

The relative concentrations and characteristics of the reactants are important in determining the relative reactivities and the stabilities of the proposed complexes. A priori, one would expect the same order of reactivity as that observed for the hypophosphorous acid studies ($4\text{-}O_2N- > 4\text{-}CH_3- > 4\text{-}CH_3O-$) for both the ease of the initial electron-transfer and the stability of the proposed association between the phenyl radical and the radical cation of TMPD. An examination of Tables 5 and 6 supports these speculations. For example, our data show that the 4-nitrobenzenediazonium ion is easily reduced. However, the data also show that other considerations are also important, in particular the pH of the solution and the procedure used to prepare the solutions.

The influences of the pH and the buffer can be explained in terms

of their importance in determining the concentrations of the reacting species of both the diazonium salt and TMPD. The possibility that a diazocompound exists in equilibrium with the diazonium ion and some other anion has been discussed in Chapter III. The only species which were present in our experiments were the buffer, TMPD, solvent and the diazonium ion. While the interaction between the diazonium ion and the buffer would be expected to be small, we cannot discount the possibility of such an interaction because of the large differences in their concentrations. The concentrations of the diazonium salt and the buffer differed by a factor of a thousand. To minimize the interaction between the diazonium ion and the buffer as well as the hydroxide ion, it would be advisable to study the reaction in strongly acidic solutions, that is, pH 1.0. However, these reaction conditions are not practical, since the TMPD exists in the diprotonated form in very acidic solutions and does not react with the diazonium salts in this form.

The proton equilibria of TMPD in water were measured in the usual manner by titrating a known weight of TMPD·2HBF$_4$ with a standardized sodium hydroxide solution. These curves indicated that the two equivalence points occur at pH's 5.2 and 8.5. Therefore, the amine exists in the monoprotonated form at pH's of our buffered solutions and chiefly as the free amine in the neutral, unbuffered solutions.

In summary, then, a strongly acidic solution would favor the diazonium salt, while a neutral solution would favor the amine. We, therefore, compromised by using solutions buffered at approximately pH 5. The effect of changes in the pH of the solution showed the expected general trend, that is, fewer radicals were produced in the more

acidic solutions for all of the diazonium salts. For example, the radical to diazonium ratios fell from 2.0 to 1.0 and from 3.0 to 2.0 for the 4-nitro- and the 4-methoxybenzenediazonium salts, respectively, when the pH's of the solutions were changed from neutral to 5.0.

The effect of changes in the procedure used to prepare the reaction vessel and medium is very striking. The general trend indicates that as our ability improved to prepare the reaction medium free from impurities and to deoxygenate the solution, then the ratios of the radical to the initial diazonium salt concentrations decreased and that a maximum concentration of the radical was observed with the use of Procedure IV. The sensitivity of the reaction to its medium is demonstrated by the lack of our ability to reproduce the experimental results. Tables 5 and 6 show many examples of duplicate experiments which should have given identical experimental results but did not. The most striking example is the unsubstituted benzenediazonium salt.

The results of our experiments with the oxidized amine, $TMPD^{(+)}ClO_4^{(-)}$, and the 4-methoxybenzenediazonium salt further indicate the complexity of the reaction. The species responsible for the decrease in the radical concentration with the increasing diazonium salt concentrations are not known at this time, but it could be the 4-methoxyphenol. While these results do show that the reaction is more complicated than a simple, initial, one-electron transfer reaction to reduce the diazonium salt to the corresponding diazo radical, these results do not show that the initial one-electron reduction is a reversible reaction. However, the reaction which is observed between the oxidized TMPD and the diazonium

ion could also be responsible for the decrease in the radical cation of TMPD concentration which is observed with the reaction between the diazonium salts and TMPD after the maximum concentration of the radical has been obtained.

Kinetic and Product Studies

Both our experimental results and those which are reported in the literature indicate that the corresponding phenol of the diazonium salt is the principal product when the diazonium salts are decomposed in an acidic, aqueous solution. However, both sources of experimental results indicate that changes in either the substituent functions of the diazonium salt or the reaction medium can drastically change the reaction pathway which is followed by the diazonium salts and, therefore, the products and kinetics which are observed. The importance of these changes in the behavior of the diazonium salts can be seen by the comparisons of the behavior of the various substituted diazonium salts to the behavior of the benzenediazonium ion with respect to the reaction medium. Comparisons of the rate constants which were calculated for identical experiments and of the rate constants which were calculated by the different mathematical methods also show the importance of these factors. The importance of the mathematical method is related to the importance of the use and errors of the initial and infinity values which were used in the calculations. The error which is introduced when the initial value is used is due, in part, to the loss of solvent during the deoxygenation process. This loss amounted to one to five ml. from a 50 ml. solution and, therefore, a possible 10 per cent error in the initial and product concentrations. The errors

which were introduced into the infinity values come from two sources. First, the base line for the special quartz cells showed large deviations in the ultraviolet region and, therefore, it was difficult to determine the exact absorption of the products. Secondly, the infinity value was found by determining the absorption of the wavelength of the absorption peak of the diazonium salt. This means that we were recording an absorption value for some wavelength which was located on the shoulder of the product absorption peak. A slight change in the products of their yields would drastically change the infinity value. Therefore, the rate constants which were calculated by the mathematical methods which did not depend on the infinity or initial values should be the most accurate.

The benzenediazonium ion is well behaved under our experimental conditions and the simple phenyl cation pathway appears to offer a satisfactory explanation for its thermal decomposition to phenol. Comparisons of the literature rate constant, Table 1, to our rate constants, Table 7, indicate excellent agreement although the pH of the aqueous solutions were not the same in both cases. The freedom from complicating factors is also demonstrated by the generally close agreement in the rate constants which were calculated by our different mathematical methods. The best agreement is obtained with the last five methods, that is, Methods g through k, which rely on neither the infinity nor the initial values. The differences between our rate constants and those which have been reported in the literature appear to be no worse than the discrepancies which have been reported by other workers. A comparison of the rate constants which were determined by DeTar[106] and those which were

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[106]DeLos F. DeTar and A. R. Ballentine, J. Am. Chem. Soc., 78, 3916 (1956).

determined by Moelwyn-Hughes and Johnson[72] shows a general discrepancy amounting to about 3 per cent, in spite of their efforts to take every reasonable precaution concerning their experimental procedure and technique. These workers could not explain the reason for these discrepancies. A similar comparison for the 4-methylbenzenediazonium ion, Table 8, also reveals that our rate constants agree with the rate constant which is quoted from the literature, Table 1, and that there is a general agreement between the rate constants which were calculated by our different mathematical methods.

However, both our results, Table 9, and the results which are found in the literature, Table 1, indicate that the behavior of the 4-nitrobenzenediazonium ion in acidic, aqueous solutions is not consistent with the simple, ionic, phenyl cation pathway's being the only important reaction pathway. Specific examples of suggested free radical reactions which have been discussed in Chapters II and III include the reactions between this diazonium ion and the bromide ion in the presence of a cuprous salt as well as the reaction with hypophosphorous acid. The activating influence of the electron-withdrawing nitro function towards possible free radical reactions is emphasized when it is replaced by the diazonium function. The 4-phenylenetetrazonium ion is said to react with the iodide ion by a free radical pathway. Our experimental evidence which suggests that free radical reactions are responsible for some of our results include the sensitivity of our experiments to oxidizing agents, such as molecular oxygen and hydrogen peroxide, and our nonreproducible kinetic results for what should have been identical experimental conditions. However, in addition to the

simple phenyl cation pathway and at this time some undefined free radical pathway, our experimental results also suggest that complex formations and a bimolecular reaction could also be important with reactions of the 4-nitrobenzenediazonium ion. If equimolar concentrations of acetic acid and sodium acetate are used as the buffer in deoxygenated solutions, 4-nitrophenylacetate is produced in a high yield. This product could arise from a bimolecular attack on the diazonium ion by the acetate anion or from the intermediate 4-nitrobenzenediazoacetate which could rearrange to the product by a six-membered ring transition state with the loss of nitrogen. Such a rearrangement has been suggested for the reaction of diazonium salts with potassium ethylxanthate.[85] Our kinetic experiments which used the iodide ion discredit a simple bimolecular attack by iodide on the diazonium ion. When this anion was added to the reaction solution, then a decrease in the first-order rate constant with respect to the diazonium salt was observed. Although our results do not permit us to define clearly this reaction, a reasonable pathway would involve an initial complex formation to form the 4-nitrobenzenediazoiodide intermediate which then gives the observed product either by attack of a second iodide ion or a cyclic rearrangement. Our kinetic experiments with 4-methoxydimethylaniline and 4-dimethylnitroanilines also suggest the importance of complex formations with this diazonium ion by the decrease in the rate of decomposition which was observed in their presence.

In summary, then, several different reaction pathways are available to the 4-nitrobenzenediazonium salt in acidic, aqueous solutions. This variety of reaction pathways and the influence of possible complexing

agents could explain our nonreproducible kinetic results. Specific examples of these discrepancies may be found by comparing the rate constants which are given for the last two experiments for this diazonium salt in Table 9. Both of these experiments were performed in monobasic potassium phosphate buffered solutions whose buffer concentrations were 0.01 M. There is not a good correlation between the rate constants which were calculated by the eleven different mathematical methods for a single experiment. The best correlations are found between the rate constants which rely on neither the initial nor the infinity values, that is, Methods g through j; the last method, k, a least squares method, does not rely on either of these quantities, but it is in poor agreement with the other results. There is no apparent reason for this discrepancy, since this method did give reliable results with the unsubstituted diazonium ion. A comparison of the rate constants which were calculated by Methods g through j with the rate constant which is found in Table 1 shows that our rate constants differ from the one which was found by Crossely, Kienle and Benbrook[71] by approximately a factor of ten. Some possible reasons for this discrepancy are that the workers used the evolution of nitrogen while we used a spectrophotometric method as the experimental means for accumulating the data which are necessary for the calculation of the rate constants, that they used higher concentrations of the diazonium salts than we did and, therefore, our studies would be expected to be more sensitive to the presence of other compounds, and that the pH's of the reaction solutions were different. Our experiments were performed at pH 5, while theirs were performed at pH 1.2. A clear, concise description is not possible at this time for the reaction pathways

which are responsible for these experimental results, but both our experimental results and those which are found in the literature clearly show that neither the simple, ionic, phenyl cation pathway nor the modifications which have been suggested by Lewis and Taft are sufficient to explain the experimental results.

The behavior of the 4-methoxybenzenediazonium tetrafluoroborate has not been investigated as extensively as the 4-nitrobenzenediazonium salt. However, our experimental results for this diazonium salt also show many discrepancies. Our rate constants which are reported in Table 10 show poor agreement in the same fashions which were discussed for the 4-nitrobenzenediazonium salt. A comparison of our rate constants with the one found in Table 1 indicates that our reactions were faster by approximately a factor of ten. However, some of our more recent experiments showed that this diazonium salt has a remarkable resistance to decomposition under our refined experimental conditions, while some of our earlier experiments showed a marked rate enhancement. The reasons for this behavior are not apparent at this time, but our results suggest that the accepted reaction pathway for the decomposition of this diazonium salt in acidic, aqueous solutions must be re-examined. Important factors which should be included in such an investigation include the presence of trace amounts of other compounds and the purity of the diazonium salt and the reaction medium.

Ultraviolet Spectra Studies

The experimental results which were obtained from our TMPD studies as well as our kinetic and product studies indicate that possibilities of complex formations between the diazonium salts and other compounds

are very important. These complex formations can influence the choice of the reaction pathway by initiating a free radical chain reaction, by forming a second, stable compound in an equilibrium with the benzenediazonium ion, and by holding the reacting species in an ideal position so that further reaction can occur. These complexes can be formed by the terminal nitrogen of the diazonium function acting as an acid to form a sigma complex or by the pi electrons of the aromatic nucleus of the benzenediazonium salt interacting with the pi electrons of another aromatic compound to form a pi complex.

Specific examples of each of these possibilities from the literature which has been discussed in Chapters II and II include the reaction between diazonium salts and the acetate anion in deoxygenated, methanolic solutions, the reaction between the diazonium salts and the iodide ion and thiophenol, the equilibria which can be established between the substituted benzenediazonium salts and the hydroxide, the sulfite and the cyanide anions, the sigma complexes which can be formed between benzenediazonium salts and the ions of the transition elements and the pi complex which can be formed between TMPD and 1,4-dinitrobenzene. Specific examples from our experimental results which illustrate the importance of these interactions include the identification of 4-nitrophenylacetate as the principal product from the decomposition of the 4-nitrobenzenediazonium salt in deoxygenated, acetate buffered solutions, the decrease in the rate of decomposition of the 4-nitrobenzenediazonium salt which is observed when the iodide ion, 4-methoxydimethylaniline, or 4-dimethylnitroaniline is added to the aqueous solution, our nonreproducible kinetic rate constants, and the very rapid reaction which is

observed between TMPD and the benzenediazonium salts. The importance of complex formation in the reaction between the benzenediazonium salts and TMPD could involve not only an initial electron transfer but also the stabilization of the intermediate reacting species.

Our first experimental approaches designed to accumulate qualitative data for the existence of complexes consisted of a direct examination of the ultraviolet absorption spectra of the reaction solutions and by an analysis of our kinetic data. The direct examinations of the ultraviolet spectra failed to reveal differences which could be attributed to a complex formation in a qualitative fashion. The reasons for this failure were that the base line of the special quartz cells which were used in the deoxygenating process showed large deviations in the ultraviolet region, that the spectra of the solutions were very complex, particularly with the TMPD studies, and that the initial reactions between TMPD and the benzenediazonium salts were too rapid to allow the recording of the spectra of the solutions before extensive reaction had occurred. The analysis of the kinetic data failed because these data were not sufficiently reproducible for what were supposed to be identical experimental conditions. Because these direct approaches failed to yield any experimental evidence for complex formations, we undertook a brief investigation to determine if experimental evidence could be found for a sigma complex between the diazonium salts and the buffers and if experimental evidence could be found for a pi complex between the diazonium salts and the less powerful, aromatic, reducing agents.

Table 11 gives our experimental results of our attempts to find experimental evidence for complex formations between the buffers, the

iodide ion and the benzenediazonium salts. We employed the same experimental technique which was used by Lewis[81] in his studies with the hydroxide, the sulfite, and the cyanide anions. He found large shifts in the positions of the absorption peaks as well as large changes in their extinction coefficients which he attributed to the formation of benzenediazo compounds. However, we observed changes only in the extinction coefficients for the experiments. Therefore, it was not possible for us to calculate equilibrium constants as Lewis did in his studies. To minimize our experimental errors in recording the spectra of the solutions we used a matched pair of one cm., glass-stoppered, Beckman quartz cells in place of the special quartz cells which were made for the deoxygenating apparatuses and recorded the spectra as quickly as was experimentally possible after mixing the reactants. We feel, therefore, that the differences in the extinction coefficients which are greater than 10 per cent are significant for solutions of the same pH.

An examination of the data given in Table 11 indicates that the unsubstituted and the 4-methylbenzenediazonium salts are not greatly affected by the presence of the other compounds. These observations agree with our kinetic and product studies.

The extinction coefficients of the other diazonium salts in the potassium iodide solutions show a relationship for the 4-substituted halo- and nitrobenzenediazonium salts. These extinction coefficients for the iodide solutions, Column 5, should be compared with the extinction coefficients which were found for the diazonium salts in solutions of the same pH but in the absence of the potassium iodide,

Column 1. The 4-iodobenzenediazonium salt solution shows a marked decrease in its extinction coefficient. The 4-bromobenzenediazonium salt shows a similar, but smaller, decrease. The 4-substituted chloro-, nitro- and methoxybenzenediazonium salts show an increase in their extinction coefficients. This order for the changes in the extinction coefficients is the same order as the increasing electronegativities of the halo and the nitro functions. The fact that the nitro and methoxy functions do not fit nicely into this scheme could be related to the manner in which they stabilize the diazonium function. The nitro function is electron-withdrawing, while the methoxy function is electron-donating towards the diazonium function.

The influence of the acetate ion is shown by the comparisons of the extinction coefficients which are found in Columns 1 and 4 as well as Columns 2 and 3. The first comparison is for solutions of pH 5.0 and it indicates that there is a general increase in the extinction coefficients for the 4-substituted halo- and methoxybenzenediazonium salts but that the 4-nitrobenzenediazonium salt shows a decrease. These changes in the extinction coefficients are consistent with equilibria of pH 5.0 established in these solutions. These equilibria probably involve the benzenediazonium ions reversibly reacting with the acetate anion to form a benzenediazoacetate. The second comparison shows that there are only small differences in the extinction coefficients in these more acidic solutions and, therefore, the equilibrium constants for the formation of the benzenediazoacetates in these solutions are probably very small. This interpretation is consistent with our experimental results and those which have been

reported in the literature. Our experimental results show that the presence of the acetate anion was important for the studies which used the 4-nitrobenzenediazonium salt but that it was not important with the unsubstituted benzenediazonium salt. The results of other workers show that the presence of the acetate anion is important in basic, aqueous or methanolic solutions, but there is no evidence in the literature that benzenediazoacetate is formed from the acetate anion and the benzenediazonium salt in acidic, aqueous solutions. However, the formation of these diazo compounds even in small concentrations in our studies is important because the decomposition of such compounds in basic solutions is known to produce radical species and because the formation of such compounds effectively reduces the concentration of the benzenediazonium ion which is usually considered to be the reacting species in acidic, aqueous solutions.

After the investigation of the possibilities that the acetate and iodide anions can form sigma complexes with the benzenediazonium salts, we turned our attention to the possibility that the benzenediazonium salts can form pi complexes with the 4-dimethylmethoxyaniline. Our kinetic studies, which used the 4-nitrobenzenediazonium salt and these two tertiary, aromatic amines, indicated that pi complexes are formed without the rapid reduction which was observed in our TMPD studies. The experimental and mathematical methods are well known for determining both the extinction coefficients, e_{BA}, and the equilibrium constants, K_{BA}, for the 1:1 molecular complexes which would be expected to be formed in our studies.[14] These methods consisted of making up several solutions of the two reactants, whose initial concentrations of the

benzenediazonium salt, BD, and the tertiary, aromatic amine, TA, were different. The absorption, d, of the new peak which is due to the complex is recorded and then BD/d is plotted versus 1/TA for several solutions. From the slope and the intercept of this plot, the extinction coefficient and the equilibrium constant can be obtained from Eq. 23.

$$\frac{BD}{d} = \frac{1}{e_{BA}} + \frac{1}{(K_{BA})(e_{BA})(TA)} \qquad \text{(Eq. 23)}$$

The successful use of Eq. 23 depends on the existence of a large difference in the initial concentrations of the benzenediazonium salt and the tertiary, aromatic amine. However, these amines are not sufficiently soluble in an acidic, aqueous solution to meet this requirement and, therefore, we were unable to obtain quantitative data for these possible complex formations under our acidic, aqueous experimental conditions. Figures 3 through 8 do offer qualitative data for such complexes.

Nuclear Magnetic Resonance Studies

The interpretation of the results of the nuclear magnetic resonance studies is made ambiguous for several reasons. The sensitivity of the Varian A-60 required that high concentrations of the diazonium salts and the potential complexing agent be used. Since the complexing agents are of low solubility in water, acetone-d_6 was selected as the medium for the spectral studies, and the change in the solvent changed the environment of the reaction, making a direct comparison impossible between these studies and our other studies. Although

techniques which employ ultraviolet and infrared spectra usually show definite peaks for the reactants as well as for the products, the peaks which are observed in a nuclear magnetic resonance spectrum may be due to a time-averaged phenomenon, and, therefore, the assignment of these peaks to a particular species is very difficult. Furthermore, the calibration of the chart paper with respect to the chemical shifts is made difficult because the Varian A-60 will drift over long periods of time.

Comparisons of the chemical shifts which are found in Table 12 for the mixtures with the chemical shifts for the diazonium salts, Table 13, and the complexing reagents, Table 14, in separate solution, show what appears to be a real change in the spectra upon mixing the reactants, in several instances. The shifts are generally small, and it is difficult to establish a criterion as to whether these shifts really represent a complex formation or merely reflect the change in some other experimental factor such as the change in the environment of the reactants. The fact that an association of some description does occur in some of the solutions is indicated by the chemical reactions which are observed when either 4-methoxydimethylaniline or TMPD is added to these acetone-d_6 diazonium salt solutions, and by the line-broadening of the 4-methoxydimethylaniline peaks, indicating the formation of free radicals in solution, which is observed when this complexing reagent is added to a dilute, deuterochloroform solution of 4-methoxybenzenediazonium tetrafluoroborate.

Comparisons of the chemical shifts for the diazonium salts, Table 13, with the chemical shifts for the corresponding nitro compounds,

Table 15, triazenes, Table 16, and anilines, Table 17, reveal that the expected trends in the chemical shifts do exist with the decrease in the electronegativities of the group which replaces the diazonium group. A brief investigation was conducted to determine if meaningful quantitative correlations could be found such as the correlations which were found to exist between the Hammett, substituent, sigma constants and the nitrogen-nitrogen bond stretching frequencies.[79] However, our investigation revealed no such useful correlations. Since nuclear magnetic resonance phenomena generally do not correlate with such simple relationships, this result was not surprising.

CHAPTER VIII

CONCLUSIONS

Our experimental work has shown that a very rapid, initial, production of the radical cation, $TMPD^{(+)}$, occurs for the reaction between TMPD and all of the diazonium salts which were investigated. The exact pathway which this initial reaction follows depends on the diazonium salt, the pH of the solution, and the procedure which was used to prepare the solutions and, therefore, our ability to remove extraneous compounds, particularly molecular oxygen. After this rapid, initial reaction a second sequence of complex reactions occurs. The important factors which influence these secondary reactions include the ones which are listed for the initial reaction as well as the presence of the radical cation, $TMPD^{(+)}$, and the presence of the phenol which is formed from the diazonium salt. The sensitivity of this reaction to its reaction medium, our nonreproducible kinetic results, and the rapid rate of reaction suggest that these reactions occur predominantly by free radical reaction pathways. However, our experimental data do not permit us to clearly define the reaction pathways at this time.

Both our kinetic and product studies and a close examination of those studies which are reported in the literature indicate that the decomposition of the diazonium salts in acidic, aqueous solutions are not simple nor as well understood as these reactions are generally considered to be. While the simple phenyl cation reaction pathway appears to describe the reaction pathway adequately for the unsubstituted and

the 4-methylbenzenediazonium salts, neither this simple phenyl cation pathway nor the modifications which have been suggested by Lewis and Taft adequately describe the reaction pathways for the substituted benzenediazonium salts which we considered in our studies. At this time it is not possible to give a clear, concise description of the reaction pathways which are responsible for the observed behavior of the substituted benzenediazonium salts, although the experimental results strongly suggest that free radical reaction pathways and possibly complex formations and the nature of the resonance interactions between the diazonium function and the other substituent in the para position must be considered as important factors for their decompositions in acidic, aqueous solutions. Any proposed reaction pathway for the decomposition of these diazonium salts must explain the profound influence of oxygen and hydrogen peroxide as well as the sensitivity of the reactions towards the experimental conditions.

Our attempts to find evidence for possible associations between the benzenediazonium salts and other species are not as definitive as one would desire because of the experimental difficulties. The studies which determined the molar, extinction coefficients of the benzenediazonium salts in the presence of the iodide and acetate anions suggest that benzenediazoiodide and benzenediazoacetate compounds are formed in an equilibrium with the reactants. Our kinetic and product studies also support the existence of associations between the diazonium salts and the iodide and acetate anions as well as with the tertiary, aromatic amines. However, at this time we cannot discount the possibility that in some cases the diazonium salts are decomposing by a radical pathway and that these

complexing reagents are acting to capture some intermediate radical species and, therefore, they can terminate the radical chain reaction.

In summary, then, both our experimental results and the results which have been reported in the literature indicate that a variety of reaction pathways are available for the decomposition of diazonium salts in acidic, aqueous solutions. Some of the reasonable pathways which one can envision closely resemble the reaction pathways which are normally reserved for the reactions of diazonium salts under other experimental conditions. For example, the reaction pathway which has been suggested for the reaction between hypophosphorous acid and the diazonium salts resembles the radical reaction pathway which has been suggested for the decomposition of diazonium salts in deoxygenated, methanolic solutions in the presence of the acetate anion. Therefore, we feel that it is important for research workers to stop thinking of the reactions of diazonium salts so much in terms of "name reactions" such as the Sandmeyer, Schiemann and Meerwein reactions and to start thinking of these reactions more in terms of the possible reaction pathways and the influence of the reaction medium on the choice of the reaction pathway or combination of reaction pathways by the diazonium salt.

CHAPTER IX

RECOMMENDATIONS

The results of our research work suggest that additional work is required to define the reaction pathways for the decomposition of diazonium salts in aqueous, acidic solutions and to explore the products and the utility as preparative methods of several reactions which have been described in this thesis. The approaches for the investigation of the possible reaction pathways will be discussed according to the experimental techniques which seem to be the best suited for the undertaking. The suggested techniques include experiments with oxygen-18 labelled water, electron spin resonance studies, further studies of reactions between diazonium salts and easily oxidized substances, complex formation studies and studies of other compounds which are structurally related to the diazonium salts. The reactions which should be explored include the alkylation-decarboxylation sequence which was used to prepare TMPD, the reactions between diazonium salts and hydrogen peroxide as well as potassium iodide.

Our kinetic studies indicate that molecular oxygen has a profound influence on the rate of decomposition for two substituted benzenediazonium salts but not for the unsubstituted and the 4-methylbenzenediazonium salts. The exact manner in which oxygen influences the reactions depends on some undefined factors. Therefore, the decomposition of the benzenediazonium salts should be carried out in oxygen-18 labelled water under a variety of experimental conditions. The oxygen-18 content

of the isolated phenol would allow the determination of the source of the oxygen, that is, either from the labelled water or from the unlabelled oxygen gas which is dissolved in the aqueous solution. The oxygen-18 content of the phenol would allow the determination of the relative importance of the simple phenyl cation pathway and some undefined radical pathway which involves the diradical, molecular oxygen. An oxygen-18 content of the phenol which is equal to that of the labelled water would indicate that only the phenyl cation pathway is important. If the oxygen-18 content is less for the phenol than it is for the water, another pathway must be considered. The experimental factors whose influence should be investigated by this technique include the pH of the solution, the influence of the substituent functions, the presence of copper salts, and the influence of easily oxidized compounds such as thiophenol, TMPD and the iodide anion.

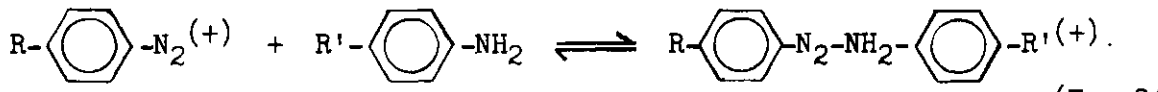
There appears to be only one study where the electron spin resonance spectral technique has been used to investigate the decomposition of a diazonium salt in an acidic, aqueous solution. In this work the presence of the phenol (the solvolysis product of the diazonium salt) and the pH of the solution appeared to be important. This technique shows promise in detecting and defining the possible free radical pathways which are apparently involved in the decomposition of some diazonium salts. However, the results of other workers indicate that the identity of the species which is responsible for the spectra which have been observed under other experimental conditions is ambiguous. A research program which is designed to determine the identity of the radical species and the influence of the reaction medium would be helpful to define the

radical pathway for the decomposition of diazonium salts in acidic, aqueous solutions.

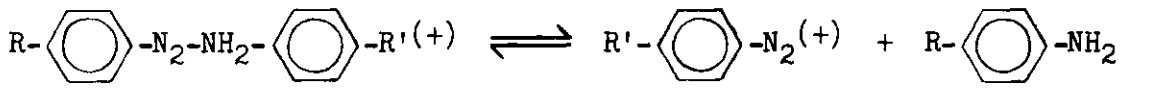
There are several accounts in the literature of reactions between the diazonium salts and easily oxidized substances. Free radical reaction pathways have been suggested for a number of these reactions because these reactions are very fast and because product studies have been very difficult to perform in either a qualitative or quantitative fashion. Examples of such reactions are the reaction between the iodide anion and the 4-phenylenetetrazonium salt[9] and the reaction between thiophenol and the diazonium salts.[8] Kinetic and product studies of these and of related reactions would be hard to perform experimentally, but they would be expected to produce useful information concerning the reaction pathways as well as to define useful preparative reactions.

Apparently, there is no evidence in the literature that diazonium salts can form pi complexes, although the associations between the terminal nitrogen of the diazonium function and a variety of compounds have been extensively investigated. The question of whether the reactions of our studies involve a pi or a sigma complex could be important to determine the choice of the reaction pathway by the diazonium salt. There are several spectral experiments which could help to clarify this question. First, other solvents besides water and mixed solvents would allow the use of higher concentrations of the potential complexing reagents and, therefore, the use of Eq. 23 and the quantitative method which was outlined in the discussion of the ultraviolet spectral studies. Secondly, other less reactive compounds could be used in these complex formation studies. The compounds which would be the most relevant are

compounds where the diazonium function is replaced by the nitro function. Thirdly, useful correlations could be expected to be found from nuclear magnetic resonance spectral studies if the newer model instruments are used which permit lower concentrations of the reactants to be used. A second experimental approach is the investigation of the possibility that exchange reactions between the diazonium salts and amines can occur. Such exchange reactions can be represented by the general equations of Eqs. 24 and 25. If an exchange is observed, an association which involves the



(Eq. 24)



(Eq. 25)

terminal nitrogen of the diazonium function is indicated. There are two experimental techniques which can be used to detect such an exchange. First, the terminal nitrogen of the diazonium function could be labelled with nitrogen-15 and after the reactants have been mixed the diazonium salt could be isolated by coupling it with an activated phenol to form an azobenzene compound. The use of a mass spectrophotometer could determine the nitrogen-15 content of the azobenzene product. Secondly, by a careful choice of the reaction conditions and of the substituent functions R and R', experiments could be designed so that the diazonium salt which was originally added to the solution could not couple to form the azobenzene compound but the diazonium salt which is formed by the exchange reaction could couple to form the azobenzene compound with a

phenol or an aromatic amine which was added to the solution. The progress of such a reaction could be followed continuously by observing the appearance of the peak which is due to the azobenzene compound. Such peaks are usually in the visible region and, therefore, the peaks of the reactants would not interfere, since they are usually located in the ultraviolet region.

The experimental techniques which have been described to this point concern themselves chiefly with the investigation of a particular diazonium salt under a particular set of experimental conditions. However, the behavior of diazonium salts depends on the possible resonance interactions between the diazonium function and the other substituent functions of the diazonium salt. For example, the 4-methoxy- function is said to stabilize the diazonium function by its electron-donating ability. The substitution of other functions for the 4-methoxy- function and quantitative correlations of the data which are obtained from the reactions of these diazonium salts have led to useful knowledge concerning their reaction pathways. Recently a number of preparative schemes have been reported for other compounds where the degree of the resonance interaction between the diazonium function and the remainder of the molecule can be controlled by the pH of the solution. An investigation of these compounds by the usual experimental techniques would prove to be rewarding, since such investigations would allow the degree of the resonance interactions to undergo a continuous change.[107,108,109]

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Several reaction sequences have been described in this thesis which offer promise as useful, preparative reactions. The alkylation-decarboxylation sequence which was used to prepare TMPD was not investigated extensively by us, but it does show promise for the N-methylation of activated amines. At this time the decarboxylation step is the least satisfactory step in the sequence. The reasons for the poor yields which have been observed for this step could include acid anhydride formations and a radical pathway. These possibilities should be investigated. A second reaction is the oxidation of the diazonium salts by hydrogen peroxide in an acidic, aqueous solution. Such oxidations of diazo compounds in alkaline medium have been extensively investigated,[3] but apparently we are the first to attempt the oxidation under our acidic experimental conditions. However, Lee, Calvert and Malmberg[55] have reported the photolysis of 4-nitrobenzenediazonium chloride in 98 per cent hydrogen peroxide solution. The aromatic hydroperoxide $4\text{-}O_2NC_6H_4O_2H$ was said to have been obtained in a chloroform solution by the extraction of the reaction mixture. When water was added to this solution, then oxygen was evolved and 4-nitrophenol was detected. No further reports by these workers have appeared in the literature concerning the possible formation of aromatic hydroperoxides which, perhaps, is a significant observation concerning the existence and the stability of these compounds. In alkaline solutions the oxidation of diazonium salts by the ferricyanide ion, the permanganate ion or hydrogen peroxide leads to the formation of arylnitramines, $ArNHNO_2$. Therefore, an investigation of the products and of the reaction pathway which are formed under our mild experimental conditions would be expected to be rewarding. Our reaction sequence could lead to a successful preparative route to the unknown

aromatic hydroperoxides. A third reaction is the reaction between the 4-nitrobenzenediazonium salt and potassium iodide in an acidic (pH 5.0), aqueous solution. This reaction should be investigated for the other diazonium salts.

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